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Journal
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Vol. 212 NOVEMBER, 1931 No. 5

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; SOME OF THEIR PHYSICAL AND CHEMICAL PROPERTIES.*

BY

CHARLES A. KRAUS, Ph.D.,

Professor of Chemistry, Brown University.

I. INTRODUCTION.

The Metallic State of Matter.—Of the 90 known elements, 72 are metals in the free or elementary condition, 4 more commonly exist in either metallic or non-metallic allotropic states, 6 are inert non-metallic elements, and only 8 are chemically active, non-metallic elements. It is also true that practically all compounds of metallic elements with one another are metallic, that many compounds of metallic with non-metallic elements are metallic, and that there are certain compounds containing only non-metallic elements that exhibit metallic properties.[1] These synthetic metals, so to speak, are not generally stable, yet they are of special significance in that they show that the property of metallicity is not necessarily an atomic phenomenon.

While metallic substances, both elementary and compound, are extremely numerous and are of the greatest importance, both from the practical and the scientific point of

* Presented at a meeting held Thursday, January 15, 1931.

[1] Kraus, *J. Am. Chem. Soc.*, 35, 1732 (1913).

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

view, it is a surprising fact that chemistry deals chiefly with non-metallic substances. This is well illustrated by the space allotted to metallic and non-metallic substances in the handbooks of chemistry. It is evident that our knowledge of metallic substances is far less extensive than is that of non-metallic substances.

Our lack of knowledge of the metals is chiefly due to the fact that matter in the metallic condition lends itself to study much less readily than does matter in the non-metallic state. The metals are in general high melting and high boiling substances that are not readily manipulated at ordinary temperatures. At the same time, while metals are often readily soluble in other metals, they are not usually soluble in non-metallic solvents. Finally, their high reflecting power renders accurate visual observations difficult.

The metals are excellent conductors of electricity but, when a current passes through them, there is no appreciable material change. In electrolytes, on the other hand, a transfer of matter accompanies the current and this enables us to gain some knowledge of their constitution. The study of electrical phenomena in metals gives us but little direct information as to their constitution.

We can often gain a knowledge of the constitution of non-metallic substances by a study of their chemical reactions, for example, we can measure their reaction rates. In the case of metals this is not ordinarily possible except when reaction takes place at the interface between a metal and a non-metal. We see, then, that the metallic state of matter is one that presents many difficulties from the experimental point of view. As a consequence, our knowledge of the metallic state is very incomplete. Certain theories have been suggested from time to time but none of them has been successful in accounting for the large body of facts relating to the metallic state. Even with the aid of the modern atomic theory, advances in our understanding of metallic phenomena have been slow.

It is evident to the most casual observer that all metals are very much alike in their external appearances. All reflect light metallically and all are rather good conductors of the electric current and of heat. The electromagnetic theory of Maxwell supplies a formal relationship between the electrical

and optical properties of metals, but it tells us nothing about their ultimate constitution.

Electron Theory of Metals.—Some thirty years ago, Riecke, Drude, and H. A. Lorentz elaborated a theory of the metallic state which was founded on the assumption that the conduction of electricity and heat in metals is effected by electrons which are common to all metals and which move about freely in a metal, much as do the molecules in a gas. This theory served to account for the influence of temperature upon electrical and thermal conductance and for the law of Wiedermann and Franz, but it led to certain other results that were clearly at variance with observed facts. More recently, Sommerfeld,[2] applying the Fermi statistics to electrons in metals, has constructed a theory that accounts for many of the properties of metals without the inconsistencies of the earlier theory. At the present time, the view is generally accepted that the characteristic properties of metals are due to the presence of electrons which are free to move within the body of the metal, although subject to certain restrictions in conformity with the statistics postulated.

Such knowledge as we have of electrons in metals is largely based on the study of their physical properties and is arrived at as a result of deduction. Observations that apply more immediately to the electrons themselves are largely lacking. Yet, if electrons exist in metals, we should expect to find phenomena, chemical as well as physical, whose interpretation would follow readily as a consequence of this postulate. Heretofore, chemical phenomena of this kind have been almost wholly wanting.

II. SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS.

A. Physical Properties.

Metallic Properties as a Function of Concentration.—Let us now discuss some phenomena of physical-chemical and chemical nature that have a bearing on the problem of the metallic state. Let me put a question: If we had a non-metallic solvent that were capable of dissolving a metallic

[2] Sommerfeld, *Zeits. f. Physik*, **47**, 1 (1928); Sommerfeld and Frank, *Reviews of Modern Physics*, **3**, 1 (1931); see also Darrow, *Reviews of Modern Physics*, **1**, 90 (1929).

element, such as sodium, for example, what would be the properties of the resulting solution? Before attempting to answer this question, I should point out that the property of metallicity is not inherent in the atoms themselves, but, rather, depends upon their state or condition. Thus, carbon in the state of graphite is a metal while in the state of diamond it is a non-metal. Again, mercury in the solid or liquid state is a metal while, in the gaseous state, it is as much a non-metal as is argon or nitrogen. Moreover, certain combinations of carbon, nitrogen, and hydrogen possess metallic properties, although none of the constituent atoms has metallic properties.[1]

Returning to our question, we might expect that if the concentration of metal in a non-metallic solvent were high, it would exhibit metallic properties; modified, perhaps, owing to the solvent, but still exhibiting optical and electrical properties such as are associated with metals. But what might we expect to happen if the concentration of metal were greatly reduced, say to one gram atom in a thousand liters of solvent? Would the metallic properties persist substantially without change, except as to magnitude, or would these properties disappear in whole or in part? The theory of the metallic state in its present form does not afford a sure answer to these simple questions; their answer must be sought in experiment.

Solutions of Alkali Metals in Liquid Ammonia.—Although, as I have already mentioned, solutions of metals in non-metallic solvents are extremely rare, such solutions nevertheless exist. Liquid ammonia and certain of its organic derivatives, the lower, primary, aliphatic amines, dissolve the alkali metals and the metals of the alkaline earths.[2] The solubility of these metals in liquid ammonia is much higher than it is in the amines, for which reason the phenomena peculiar to these solutions are best studied in ammonia. The alkali metals are exceedingly soluble in liquid ammonia; one atom of lithium (7 grams) is soluble in 3.6 mols (61 grams) of ammonia.

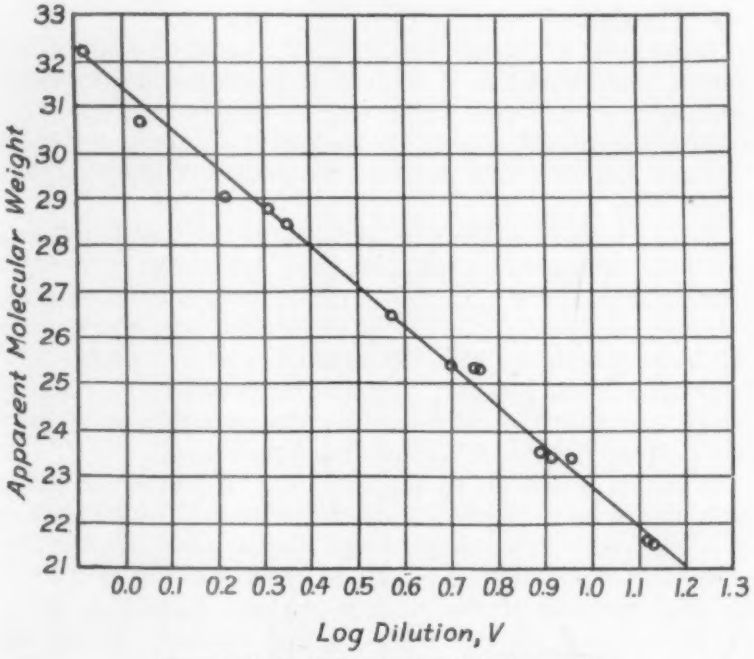
The solutions of the metals in liquid ammonia have a characteristic blue color by transmitted light when dilute, and this color is the same for all metals. The concentrated solutions exhibited metallic reflection, somewhat of a copper

[2] Kraus, *J. Amer. Chem. Soc.*, **29**, 1557 (1907).

color. The solutions of the metals are "true solutions" and not colloidal solutions as some have suggested. They closely resemble solutions of ordinary salts of the same metals.

Molecular Weight.—The molecular weight, or more correctly, the apparent molecular weight of sodium dissolved in liquid ammonia has been determined.[4] Such molecular weight determinations cannot be interpreted unambiguously, but we may say that the apparent molecular weight of sodium decreases with decreasing concentration and approaches a value less than its atomic weight. As is evident from Fig. 1,

FIG. 1.



Apparent molecular weight of sodium in liquid ammonia.

the apparent molecular weight of sodium falls to a value less than 23, its atomic weight, at a concentration of 0.1 normal and the value is tending rapidly toward lower values at still lower concentrations. A comparison of the apparent molec-

[4] Kraus, *J. Amer. Chem. Soc.*, **30**, 1197 (1908).

ular weight of sodium with that of sodium salts, such as sodium bromide, for example, indicates a similar behavior in the case of these two substances at lower concentrations. According to present views, which seem well substantiated, such a solution of sodium bromide is largely, if not completely, dissociated into its ions, even at fairly high concentrations. This accounts for the fact that the apparent molecular weight of salts at lower concentrations is less that the formula weight. By analogy, then, the low value of the apparent molecular weight of sodium may be ascribed to an ionic dissociation of the sodium atoms. It becomes an interesting problem to determine the nature of the ions that result when an atom of a metallic element dissociates.

Electrolysis of Metal Solutions.—As early as 1897, Cady showed that solutions of sodium in ammonia are excellent conductors of the electric current.[5] He showed, too, that polarization effects appear to be absent in these solutions. This fact suggests that these solutions may conduct metallically.

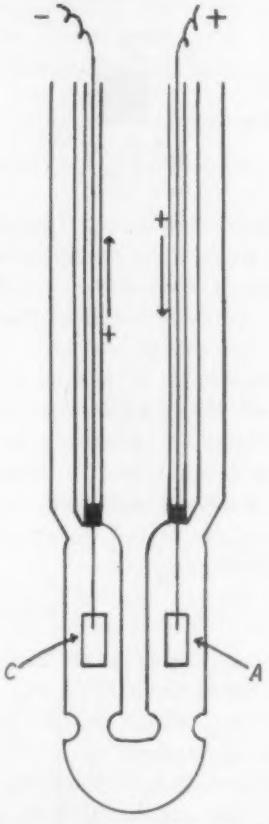
If an atom of sodium (or potassium) is dissociated into ions in liquid ammonia solution, then, under the action of a potential, these ions must move, the moving ions constituting a current of electricity. At the electrodes, which are generally impermeable to ions, accumulation of the products of electrolysis should occur. In this connection, it may be pointed out that the color of the metal solutions serves as a very delicate indicator of concentration change.

If a cell is set up as shown in Fig. 2 and a current of electricity is sent through a dilute solution of potassium in ammonia, between the anode *A* and the cathode *C*, we find that there is an immediate and marked concentration of color in the neighborhood of the cathode surface, indicating an increased concentration of metal in that region.[6] In the immediate neighborhood of the anode surface *A*, the solution becomes colorless, the colorless layer having a thickness of the order of 0.1 mm. or less. If the process of electrolysis is continued for some time, the color is completely transferred

[5] Cady, *J. Phys. Chem.*, 1, 707 (1897).
[6] Kraus, *J. Amer. Chem. Soc.*, 30, 1323 (1908).

from the anode to the cathode compartment. The current, of course, diminishes during this process owing to depletion of the solution of ions in the anode compartment. If the direction of the current is reversed, the direction of color change is also reversed. Since the density of color increases only with

FIG. 2.



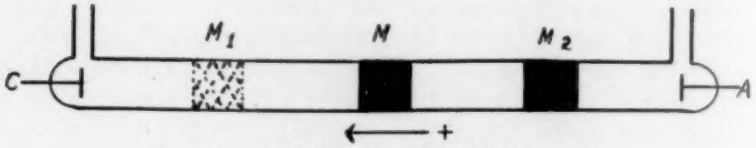
Cell used in electrolysis of metals in liquid ammonia.

increasing concentration of free metal, this experiment shows that the process of conduction in these solutions is an ionic one and that the potassium atoms (or ions) are transferred in the direction of the positive current. They must, therefore,

be positively charged. We might say, then, that the metal is carried in the direction of the positive current. This, however, is not strictly true, as a second experiment will show. This experiment, too, will make clear what a metal really is.

Transfer of Electrons.—Let us suppose that we have a long tube, as shown in Fig. 3, provided with electrodes *A* and

FIG. 3.



Illustrating the transfer of metal by the electric current.

C, and let us introduce at *M*, near the middle of the tube, a few centimeters (length) of a solution of potassium in ammonia. This solution is represented by the crosshatched area of the figure at *M*. To either side of the potassium solution, and filling the tube up to the electrodes, let us introduce a solution of potassium amide in liquid ammonia. Potassium amide, KNH_2, is an electrolyte that resembles potassium hydroxide and is related to ammonia in the same way that potassium hydroxide is to water. Potassium amide is dissociated in liquid ammonia solution into positive ions K^+ (potassium ions) and negative ions, NH_2^- (amide ions), according to the reaction equation:

$$KNH_2 = K^+ + NH_2^-.$$

Now let us apply a potential to the electrodes such that the positive current flows from *A* to *C*, as indicated by the arrow. I should state, here, that the potassium solution is colored blue while the potassium amide solution is transparent and practically colorless. By observing the motion of the colored solution we can easily determine whether the free metal is carried in the direction of the positive current or in the reverse direction.

In the preceding experiment, we saw that the metal was carried from the anode to the cathode compartment, that is, in the direction of the positive current. We might expect, therefore, that the blue solution in the second experiment

would similarly be carried in the direction of the positive current, that is from M to M_1. Actually, however, we find that the metal is carried in the opposite direction, the blue color travels in the direction of the negative current.[7] After a time it is found at M_2 as shown in Fig. 3. Now, how are we to account for the apparently contradictory results of these two experiments?

The Metallic Constituent of Metals.—In experiment 1, the concentration of free metal increased around the electrode toward which the positive current flowed (the cathode), while in experiment 2, the free metal unquestionably traveled in the direction in which the negative current flowed, that is, toward the anode. The explanation is simple. *The positive constituent of a metal has no metallic properties, the negative constituent, only, imparts to a metal those properties that we call metallic.* Both experiments 1 and 2 show conclusively that in solutions of metals (at least in dilute solutions) the current is carried by oppositely charged ions, one of which is the positive ion of the metal while the other is a negative ion which is the same for all metals. It has been shown that the positive ion of a metal in solution is idential with the positive ion of a salt of the same metal. The negative ion is the electron, e^-. When a metal, potassium, for example, dissolves in liquid ammonia, it goes into solution as the ions K^+ and e^- thus:

$$K \times NH_3 \rightarrow K^+ + e^- \text{ (solution)}.$$

The electron ion, e^-, is the same for all metals in liquid ammonia solution. The same electron exists in the metals prior to solution and the metals owe their metallic properties to these electrons. The electron is the metallic constituent of all metals and it is to the electron that metals owe their metallic properties.

Let us now interpret experiment 1. It appeared that in this experiment the metal was carried from electrode compartment A to compartment C; and so it was. But the metal was not carried from A to C through the solution, it was only the non-metallic constituent, the K^+ ion, that was so carried. The metallic constituent, e^-, the electron, was carried from A

[7] Kraus, *Ibid.*, 30, 1342 (1908).

to *C*, not through the solution but through the external electrical circuit. Under the action of the applied potential, electrons pass into electrode *A* from the surrounding solution, then through the external metallic circuit and, finally, they re-enter the solution through the electrode *C*. In the external circuit, the current is carried entirely by electrons, in the solution, the current is carried in part by electrons, moving toward *A*, and in part by K^+ ions, moving toward *C*. The cathode *C* is impervious to K^+ ions and these ions therefore accumulate at the surface, but, as they collect, an equivalent number of electrons enters the solution from *C* so as to maintain electrical equivalence.

The interpretation of experiment 2 now becomes clear. The positive ions, K^+, of the metal solution at *M* move in the direction of the positive current They are preceded by the K^+ ions of the potassium amide solution to the left and are followed by the K^+ ion of the potassium amide solution to the right. There is nothing of a metallic nature involved in this process, it is a purely electrolytic one. But consider the electrons: The electrons e^-, being negatively charged, move in the direction of the negative current, to the right. They are preceded by the negatively charged NH_2^- ions on the right and are followed by the same ions on the left. Thus, as time goes on, the electrons, which constitute the metallic constituent of metallic postassium, move further and further to the right. We see, then, that experiments 1 and 2 are in accord. The apparent contradiction between them was due to the fact that we wrongly attributed metallic properties to the positive ion of potassium, whereas, it is the negative constituent, the electron, to which metallic properties are due.

Relative Carrying Capacity of the Electrons and the Sodium Ion.—I have stated that in experiment 1 the current in the metal solution was carried in part by positive ions and in part by electrons, the two, of course, moving in opposite directions. If this is true, then it should be possible to determine the proportion of the total current carried by these two ions. Such determinations may be accomplished by means of transference measurements, in which the concentration changes, resulting at the electrodes on passage of the current, are determined by analysis. Such measurements can not well

be made in the case of the metal solutions in liquid ammonia. The transference numbers of the ions, that is, the fraction of the total current carried by them, can more readily be determined by measuring the electromotive force of concentration cells with transference. Such cells comprise two solutions of different (known) concentrations, both of which are provided with identical electrodes, permeable with respect to one of the ions and impermeable with respect to the other. The electromotive force of such a cell is given approximately by the Nernst equation:

$$E = \frac{nRT}{F} \log_e \frac{C_1}{C_2}.$$

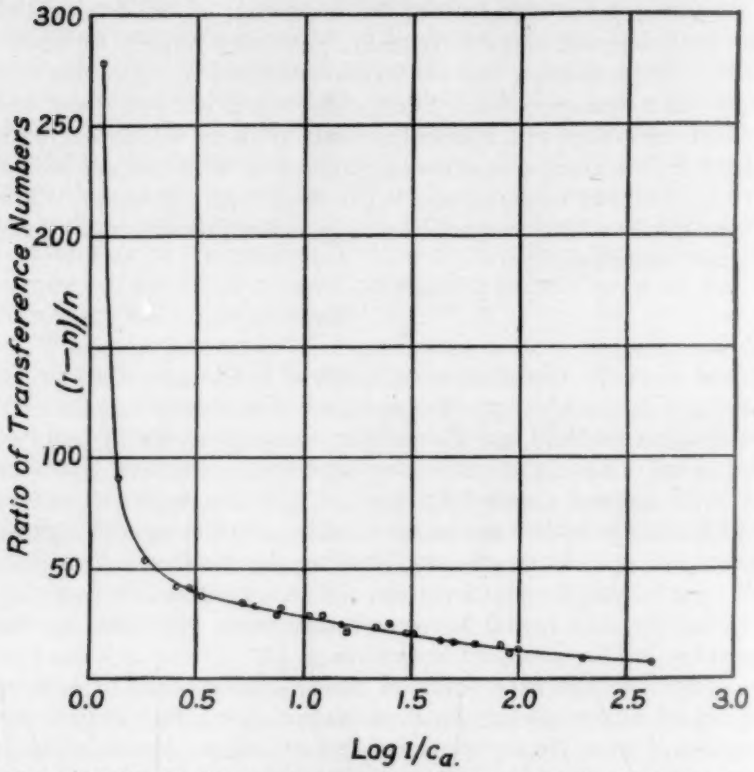
When E is the electromotive force, R is the gas constant in joules, T is the absolute temperature, F is the electrochemical equivalent and C_1 and C_2 are the concentrations of the two solutions. The factor n is the transference number (fraction of total current carried by ion) of that ion with respect to which the electrodes are impermeable. In the case of sodium solutions, the electrodes are impermeable to the sodium ions and permeable to the electrons. It is a remarkable fact that practically any metal serves as reversible electrode in the metal solutions in liquid ammonia.

The electromotive force of concentration cells of sodium in liquid ammonia has been measured at various concentrations and from these data has been calculated the fraction of the current, n, carried by the positive ions at different concentrations.[8]

In Fig. 4 are plotted values of the ratio $(1-n)/n$ of the carrying capacity of the negative ion (electron) to that of the positive ion (sodium), logarithms of the reciprocal of mean concentration of the solutions being plotted as abscissas. It will be noted that, as the concentration decreases, the value of $(1-n)/n$ approaches a limiting value of approximately 7. That is, at low concentrations, the negative carriers, the electrons, have 7 times the carrying capacity of the positive ions, or, in other words, since the two ions have the same charge, the mean speed of the electrons is 7 times that of the sodium ions.

[8] Kraus, *J. Amer. Chem. Soc.*, **36**, 864 (1914).

FIG. 4.



Showing how the ratio of the transference numbers of electrons and sodium ions varies with concentration.

Upon these results, we can base an interesting calculation. The conductance due to the electrons is 7 times that due to the sodium ions. If we can determine the conductance of the sodium ions by other means, then we can calculate the conductance of a sodium solution. Now the conductance of the sodium ion, as derived from measurement of the conductance and the transference numbers of ordinary salts dissolved in liquid ammonia, is 130. Therefore, the conductance due to the electrons (in dilute solution) should be $7 \times 130 = 910$ and the total conductance of the sodium solution should be $910 + 130 = 1040$. As we shall see presently, this calculated value is in excellent agreement with the directly measured value.

I should call attention to one other characteristic of the curve representing the relation between the relative conducting power of the two ions and the concentration. It will be noted that, as the concentration increases, the relative conducting power of the electrons increases, at first, slowly and then more and more rapidly. If the positive ion is a sodium ion, we have reason for believing that its carrying capacity is substantially independent of concentration. Therefore, with increasing concentration, the mean speed of the electrons increases very greatly. Thus, at very low concentrations, the mean speed of the electrons is 7 times that of the sodium ions; at 0.1 normal, it is approximately 30 times and, at 1.0 normal 300 times that of the sodium ions. In other words, at normal concentrations, the negative carrier has 50 times the carrying capacity that it has at very low concentrations.

The low conducting power of electrons at low concentrations might be accounted for by assuming that they are to a large extent associated with ammonia molecules. As the concentrations of electrons increases, some of them become free and move as they do in metals, carrying no matter with them other than their own inappreciable mass. These, therefore, would have a very high speed and it follows that the conductance of such solutions should be very great. We shall see that such is actually the case. It may be pointed out in passing that it can be shown that at higher concentrations a considerable fraction of the current is carried by electrons unassociated with ammonia molecules.

The Conduction Process in Dilute Solutions.—In the light of these considerations, it becomes clear what happens when a current passes between a pair of electrodes in a dilute solution of potassium in ammonia, as in experiment 1. The positive ion moves away from the anode while the electrons move into the anode. The color, therefore, disappears from the solution right at the anode surface. Practically the whole applied potential falls on this ion-free layer. At the surface of the cathode, the potassium ions accumulate, being met by the counterstream of electrons entering the solution from the cathode. The cathode process is not, however, a surface phenomenon. As the concentration of positive and negative ions increases the relative carrying capacity of the electrons increases, so

that relatively more and more of the current is carried by the electrons as we approach the cathode surface. Some of the positive ions, therefore, never reach the cathode surface at all. If the solution at the cathode becomes very concentrated, practically none of the positive carriers actually moves up to the cathode. The conduction process is then metallic near the cathode surface.

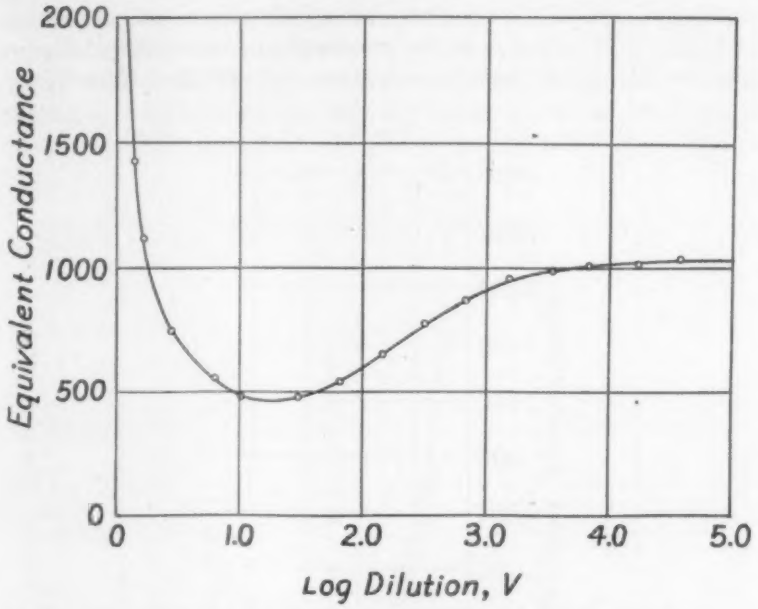
We have now answered one of the questions that we asked at the beginning, namely: what would be the properties of a solution of a metal in a non-metallic solvent. Such a solution is not actually a metal, for, in such a solution, a portion of the current is carried by the positive ions and, to that extent, the process is an electrolytic one. On the other hand, the greater proportion of the current is carried by electrons and in that respect the system is metallic. But in dilute solution, this process is qualified owing to the fact that the electrons are slowed down by the solvent molecules and the latter are perhaps carried along by the electrons. The electronic process at the electrodes is, however, a purely metallic one, for the electrons pass into and out of the electrodes without hindrance.

The Electrical Conductivity of Dilute Metal Solutions.—We can gain some further support for our conclusions from an investigation of the conductance of metal solutions at various concentrations. The conductance is readily measured by conventional methods. What we are actually interested in is the equivalent, or atomic conductance, which is the specific conductance divided by the concentration (in gram atoms per cubic centimeter). This (the atomic conductance) enables us to compare the conducting power of a given quantity of metal at different concentrations or under otherwise variable conditions.

In Fig. 5 is shown the atomic conductance of sodium as a function of concentration.[9] It will be noted that, beginning at 1/20 normal, the conductance increases as the concentration decreases and that it approaches a limiting value of approximately 1016 at very low concentrations. This value is in good agreement with the value 1040, as calculated from transference measurements.

[9] Kraus, *J. Amer. Chem. Soc.*, 43, 749 (1921).

FIG. 5.



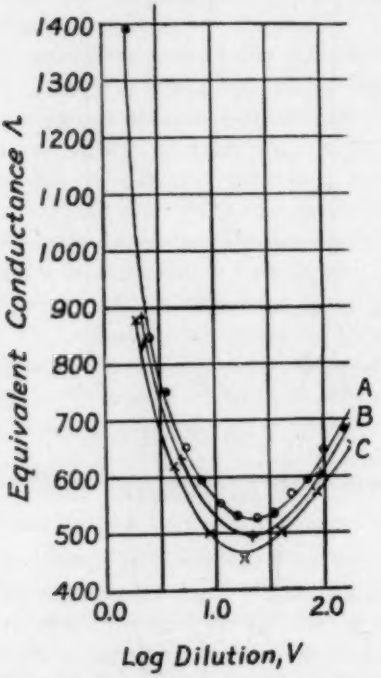
Illustrating the variation of conductance with concentration for dilute solutions of sodium in liquid ammonia.

It is interesting to examine the conductance curves of metals other than sodium. Such curves are shown for lithium (*C*) and potassium (*A*), as well as for sodium (*B*), in Fig. 6. It will be noted that the curves are similar and that the curve for sodium lies intermediate between those for lithium and potassium. This is what we should expect if the negative carrier were the same for the three metals, in which case the difference in conductance for these metals would be due to the difference in the conducting power of lithium, sodium and potassium ions. For these ions the conductance (at low concentration) is respectively: 112, 130 and 168, which corresponds approximately, at least, with the relative position of the three curves in Fig. 6.

The Conductivity of Concentrated Metal Solutions.—The conductance curve at higher concentrations presents several points of interest. It will be noted (Fig. 5) that, at 1/20 nor-

mal, the conductance has a minimum value which is somewhat less than one half the conductance at very low concentrations. At higher concentrations, the conductance increases, the more rapidly, the higher the concentration, as is evident from Fig. 7.

FIG. 6.



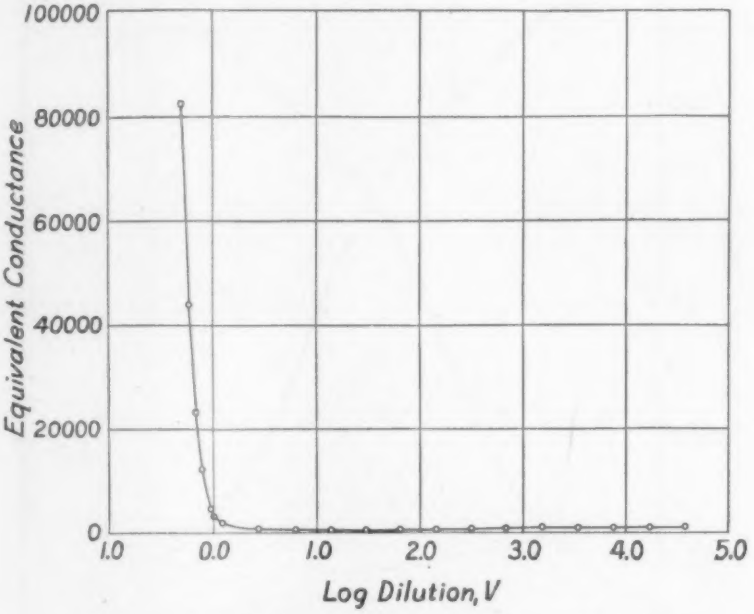
Conductance of potassium, sodium and lithium, compared.

At normal concentration, the conductance of sodium is, in round numbers, 3000 and at 2 normal it is approximately 80,000. It is evident that, in concentrated solutions, the conductance reaches values far beyond that of any known electrolytic solutions and even approaches that of metals. The increase in conductance at higher concentrations is again in agreement with the observed increase in the transference number of the electrons. We have seen that, at higher concentrations, the carrying capacity of the electrons increases enormously with respect to that of the sodium ions. Assum-

ing the conductance of the sodium ion to remain substantially constant, the conducting power of the solution must increase greatly with increasing concentration.

With Dr. W. W. Lucasse, now of the University of Pennsylvania, I measured the specific conductance of sodium and potassium solutions up to their saturation point.[10] The con-

FIG. 7.



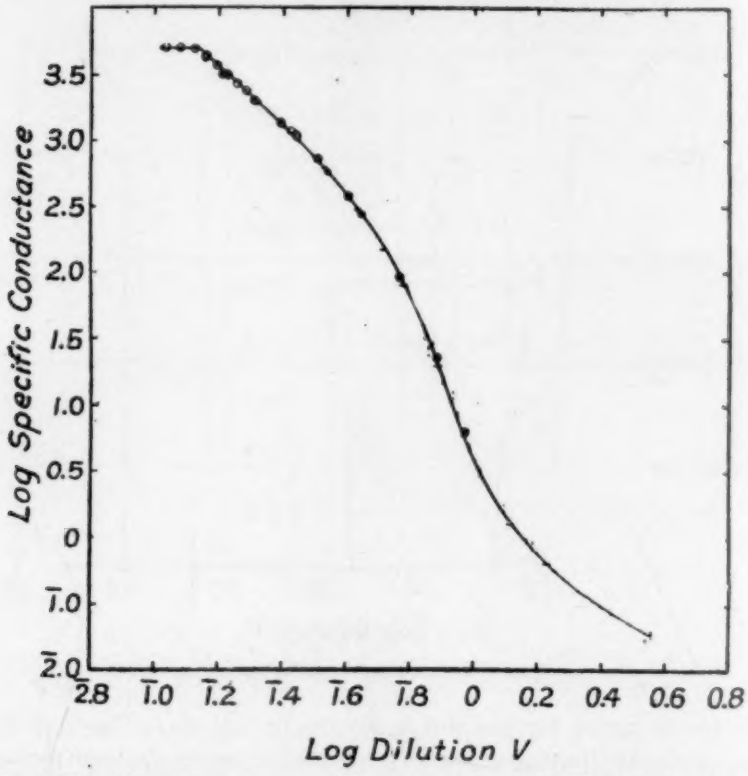
Showing the increasing conductance of sodium at higher concentrations.

ductance curve for sodium is shown in Fig. 8. The specific conductance increases rapidly with increasing concentration until at the saturation point (at $-33.5°$) it has a value of 5047 reciprocal ohms. The specific conductance of mercury at 20° C. is 10,440 reciprocal ohms. Thus, the specific conductance of a saturated sodium solution is one-half that of mercury. Clearly, these concentrated solutions are true metals. When one takes into account the fact that the concentration of sodium in these solutions is low compared with that in the

[10] Kraus and Lucasse, *J. Amer. Chem. Soc.*, 43, 2529 (1921).

pure metal, the atomic conductance reaches very high values. Thus, the atomic conductance of a saturated sodium solution is 8.73×10^5 as compared with 48.4×10^5 for metallic sodium. In other words, atom for atom, the pure metal conducts only about five times as well as its saturated solution in liquid

FIG. 8.



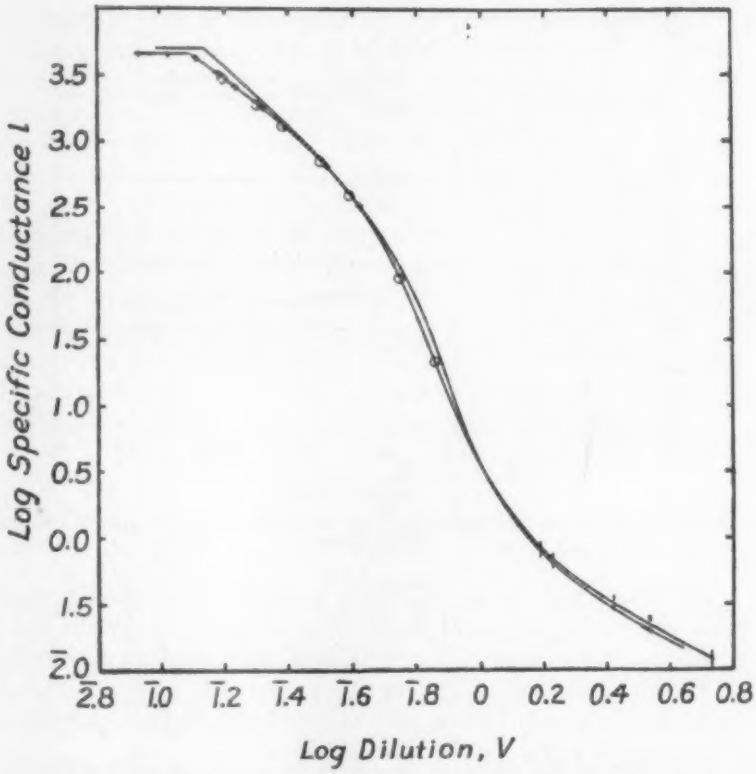
Showing how the specific conductance of sodium solutions varies up to the saturation point.

ammonia. The conductance curve for potassium (passing through points as plotted) is almost identical with that of sodium, as may be seen from Fig. 9. This shows, as clearly as anything could, the independence of the properties of these solutions of the nature of the positive ions.

Conductance-Temperature Coefficient.—The influence of temperature on the conductance of metal solutions is also very

interesting. As is well known, the resistance of metals, in general, increases with the temperature while that of electrolytes decreases. The temperature coefficient for metals is about 0.38 per cent. per degree, while that of electrolytes is several per cent. per degree, being about the same as that of the

FIG. 9.

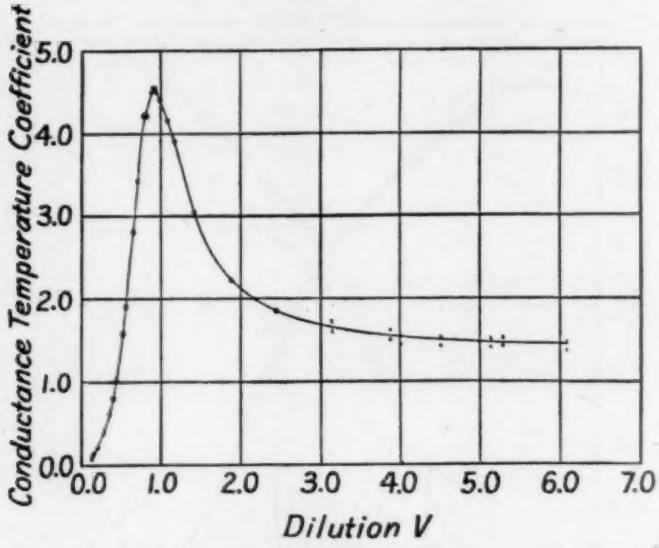


Conductance of concentrated solutions of sodium and potassium, compared.

temperature-viscosity coefficient of the pure solvent. For potassium, the resistance-temperature coefficient has a value of 1.42 per cent. at a concentration of about 0.1 normal. With increasing concentration, the coefficient increases, reaching a maximum of 4.55 per cent. At still higher concentrations, the coefficient diminishes very rapidly, reaching a value

of 0.044 per cent. for the saturated solution.[11] The curve is illustrated in Fig. 10. At the highest concentrations the metal solutions in ammonia are rapidly approaching a state closely approximating that of pure metals.

FIG. 10.



Showing how the conductance-temperature coefficient varies with concentration in the case of potassium.

Although the metal solutions in liquid ammonia present other interesting physical properties, we cannot take the space to discuss them here. Enough has been said to show that these solutions form a link between metallic and electrolytic conductors and that they owe their characteristic properties to a common ionic species, the electron.

B. CHEMICAL PROPERTIES.

Metathetic Reactions.—If the solutions of the metals contain electrons as ions, then we may expect to find chemical properties of these solutions that depend upon the presence of electrons and a study of such properties should throw light on

[11] Kraus and Lucasse, *J. Amer. Chem. Soc.*, **44**, 1941 (1922); **45**, 2551 (1923).

the behavior of electrons as chemical agents. It should be stated at the outset that electrons in ammonia are not identical with electrons as they exist in the free metals or in a vacuum tube, for example. The properties of electrons, like those of other atomic or ionic species, are modified by their environment. No ionic species can be considered without reference to the solvent medium in which it is imbedded and the same is true of electrons.

However, we may expect to find certain chemical properties of metal solutions that depend on the electrons and which, therefore, will be the same, irrespective of the metal from which they may have been derived. We have seen that the metals, in solution, are ionized into positive ions and electrons. The positive ions are identical with the positive ions of salts of the same metal while the negative ions (electrons) are the same for all metals. Now the salts of metals are also ionized and we should therefore expect that reactions of the metals with one another or with salts would be governed by the same laws as reactions of salts with other salts. If we treat a salt of one metal and a given acid with a salt of another metal and another acid, we have a metathetic reaction thus:

$$M_1X_1 + M_2X_2 = M_1X_2 + M_2X_1.$$

Actually, all the constituents are present in solution in ionic form and our solution simply consists of the four ionic species M_1^+, M_2^+, X_1^- and X_2^-. These ions undergo no reaction in solution. Reaction occurs only when the solution becomes saturated with respect to one of the four molecular species M_1X_1, M_1X_2, M_2X_1, or M_2X_2. Under these conditions, reaction proceeds until equilibrium is reached.

Precisely the same thing happens in the case of metal solutions. If we add metallic potassium to a solution of sodium chloride in liquid ammonia, we have present the ionic species Na^+, K^+, Cl^-, and e^-, where e^- represents the electron. Ordinarily, no reaction occurs and we obviously cannot say that the solution contains metallic sodium and potassium chloride or metallic potassium and sodium chloride, for both sodium and potassium are present as ions and their relation to the chloride ions and to the electrons is equal. The metallic constituent of the solution is the electron, and it makes no

difference what other ions, positive or negative, may be present. If, however, we were to concentrate the solution, we should finally reach a point where potassium chloride would begin to precipitate, for it is the least soluble of the four molecular species Na, K, NaCl and KCl. Thus, there would be left in solution a greater proportion of sodium ions than of potassium ions and, if the solvent were finally evaporated completely, the residue would contain the electrons, chiefly in combination with sodium ions as metallic sodium.[12] The reaction equation may be written:

$$Na^+ + Cl^- + K^+ + e^- \rightarrow KCl + Na^+ + e^- \rightarrow Na.$$

We commonly find it stated that, to reduce a metal from its salts, a more strongly electropositive metal is required. This, obviously, is not the case in these metallic solutions. If, for example, we treat a solution of sodium bromide with metallic magnesium, which is much less electropositive than sodium, the sodium is reduced to the metal in solution, from which free metal may be obtained by simply evaporating the solvent.[13] Written ionically, reaction occurs as follows:

$$2Na^+ + 2Br^- + Mg^{2+} + 2e^- \rightarrow 2Na^+ + 2e^- + MgBr_2.$$

The reaction proceeds from left to right because magnesium bromide is difficultly soluble in liquid ammonia and it proceeds as indicated even though magnesium is only slightly soluble.

A similar reaction occurs with a number of the less electropositive metals whose solubility in liquid ammonia is quite inappreciable.[14]

If metallic aluminum is treated with a solution of potassium amide in liquid ammonia, the following reaction takes place, again written in ionic form:

$$3K^+ + 3NH_2^- + Al^{3+} + 3e^- \rightarrow 3K^+ + 3e^- + Al(NH_2)_3.$$

The reaction proceeds from left to right because aluminum amide has a very low solubility and, moreover, is very feebly ionized. Reactions such as these occur because, despite the

[12] Kraus and Kurtz, *J. Amer. Chem. Soc.*, **47**, 43 (1925).

[13] Bergstrom, *J. Amer. Chem. Soc.*, **48**, 2848 (1926).

[14] Bergstrom, *J. Amer. Chem. Soc.*, **45**, 2788 (1923); **47**, 1836 (1925); **50**, 652 (1928).

low concentration of electrons and positive ions of the reducing metal, the latter ions are removed by reaction with a second ionic species as rapidly as they go into solution.

Other types of metathetic reactions take place.[12] If, for example, we treat silver iodide with metallic sodium in liquid ammonia, the following reaction occurs:

$$Ag^+ + I^- + Na^+ + e^- \rightarrow Na^+ + I^- + Ag,$$

or, otherwise stated, metallic silver is precipitated.[15] The mechanism of the reaction consists in the combination of silver ions with electrons to form neutral silver atoms, which, being insoluble, are precipitated.

Reduction of Negative Elements.—There is a second, extensive and important class of reactions in which the electrons take part. The atoms of strongly electropositive elements have but a low affinity for electrons, for which reason they lose their normal valence electrons when dissolved in liquid ammonia and form positive ions. The atoms of strongly electronegative elements, on the contrary, have a high affinity, not only for the electrons that they normally possess, but, also, for additional electrons, one or more depending upon their negative valence. If a negative element is treated with electrons it goes into the state of a negative ion.[12] Thus, if iodine is treated with sodium in liquid ammonia, it reacts with electrons to form iodide ions according to the equation:

$$I_2 + 2Na^+ + 2e^- \rightarrow 2Na^+ + 2I^-.$$

A similar reaction occurs in the case of sulfur, we have:

$$S + 2Na^+ + 2e^- = Na_2S.$$

Here, the sulfide ion is precipitated as sodium sulfide, because sodium sulfide is insoluble. If, however, we had employed two atoms of sulfur, we should have obtained the reaction:

$$2S + 2Na^+ + 2e^- = 2Na^+ + S_2^{2-}.$$

A disulfide ion is formed under these conditions, which remains in solution, since sodium disulfide is soluble.[16] By

[15] Burgess and Smoker, *J. Amer. Chem. Soc.*, **52**, 3573 (1930).
[16] Bergstrom, *J. Amer. Chem. Soc.*, **48**, 146 (1926).

using larger proportions of sulfur, higher sulfides, known as polysulfides may be obtained in solution. The formation of the polysulfides is actually due to a secondary reaction, since the same sulfides are obtained by merely treating the normal sulfide with sulfur, reaction taking place as follows:

$$Na_2S + S_x \rightarrow Na_2S_{x+1}.$$

Thus far, in illustrating the action of electrons on negative elements, I have only been restating the known and the obvious, for we know that the alkali metals combine directly with negative elements such as sulfur and iodine. My purpose is to make clear the mechanism of this type of reaction and then proceed to cases that are less familiar and obvious.

Negative Lead Ions.—If metallic lead is introduced into a solution of metallic sodium, reaction occurs and the lead goes into solution.[17]

If an excess of lead is present, nine atoms of lead are dissolved per atom of sodium in solution. The solution is opaque-black when concentrated and green (by transmitted light) when dilute. If the solution is evaporated, a metallic alloy is left behind and, if ammonia is again added, the alloy dissolves. Now, what is really taking place in the case of lead? The reaction is precisely analogous to that between sodium and sulfur, for, although lead ordinarily functions as a positive element, it also has a marked affinity for electrons and tends to form negative ions. Since the negative valence of lead is 4, we should expect that one lead atom would combine with four electrons. The reaction that occurs is the following:

$$Pb + 4Na^+ + 4e^- \rightarrow Na_4Pb.$$

The normal plumbide, Na_4Pb, is not very soluble and is precipitated. But, as in the case of sulfur, the lead ion tends to combine with additional lead atoms to form a polyplumbide anion, the sodium salt of which is soluble. In the presence of excess lead, we thus have the reaction:

$$Na_4Pb + 8Pb \rightarrow 4Na^+ + Pb_9^{4-}.$$

[17] Joannis, *Comp. rend.*, 113, 797 (1891); 114, 595 (1892); Kraus, *J. Amer. Chem. Soc.*, 29, 1557 (1907); Smyth, *J. Amer. Chem. Soc.*, 39, 1899 (1917).

The solution contains positive sodium ions, Na^+, and negative polyplumbide ions, Pb_9^{4-}. We should expect such solutions to behave like solutions of electrolytes. This may at first appear surprising, for compounds of sodium and lead are well known, and it is also known that these compounds are metallic alloys. Metallic alloys are not ordinarily supposed to be salts. But, while the result is unexpected in the light of prevailing conceptions, which have, perhaps, been unduly influenced by the accident of our surroundings, experiment shows that solutions of sodium polyplumbide possess all the properties of electrolytic solutions and none of the properties of metallic solutions.

To show that a solution of sodium polyplumbide is an electrolytic one, we have only to electrolyze such a solution between lead electrodes. If the solution is an electrolyte, lead will be precipitated on one of the electrodes; and, if lead forms the anion, lead will be precipitated on the anode and dissolved at the cathode. This is, in fact, what occurs. For every equivalent of electricity passing through the solution, 2–1/4 atoms of lead are dissolved at the cathode and precipitated on the anode. We, obviously, do not have 2–1/4 atoms of lead associated with a unit of negative charge; what we do have is $4 \times 2\text{–}1/4$, or 9 atoms, of lead associated with four negative charges.

Not only lead, but the elements of the fourth, fifth, and sixth groups of the periodic system, form salts of the polytype [18] and these salts are metals in the pure state in the case of the heavier elements. Certain of the intermetallic compounds, therefore, lose their metallic properties when they are dissolved in a non-metallic solvent. This bears out a statement that was made earlier to the effect that metallic properties are dependent upon condition and, particularly, the proximity of atoms to one another.

In the present discussion, the chemical properties of electrons in liquid ammonia solution have been touched upon only briefly. Space does not permit of a more extended treatment. The electrons constitute the most reactive reducing agent that we have at our disposal under ordinary condi-

[18] Kraus, *J. Amer. Chem. Soc.*, **44**, 1216 (1922); *Trans. Amer. Electrochem. Soc.*, **45**, 175 (1924).

tions. They react with many elements, in the compound state as well as in the elementary condition. The use of metal solutions as reagents opens up an extensive field of chemistry, which, as yet, has hardly been touched.

III. CONCLUSION.

The alkali metals and the metals of the alkaline earths dissolve in liquid ammonia with the formation of ions. The positive ions are the normal ions of these metals while the negative ions are electrons. The physical and chemical properties of these solutions are in accord with this view.

Metallic compounds, when they dissolve in liquid ammonia, form ions of the normal type. The more electronegative element forms the anions.

The metallic condition of matter is restricted to matter in a highly condensed state. If the atoms are separated, whether in solution or as a vapor, the metallic properties disappear. In an ionizing medium, however, the electron retains certain of the properties that it possesses in elementary metals.

CLASSICAL ELECTRODYNAMICS AND THE CONSERVATION OF ENERGY.

BY

W. F. G. SWANN,

Director of the Bartol Research Foundation of The Franklin Institute.

BARTOL RESEARCH FOUNDATION
Communication No. 61.

Many years ago, Abraham raised a difficulty concerning the conservation of energy as applied to the Lorentzian electron. Briefly, the difficulty was as follows: The fundamental postulate of Lorentz was to the effect that the electron moves in such a way that

$$\int\int\int \left(\mathbf{E} + \frac{[\mathbf{uH}]}{c} \right) \rho d\tau = 0, \qquad (1)$$

where $\mathbf{E}$ and $\mathbf{H}$ refer to the total field, $\mathbf{u}$ to velocity, ρ to density, and $d\tau$ to the element of volume. Dividing the integral into two parts, one involving the external field $\mathbf{E}_0$, $\mathbf{H}_0$, and the other involving the field $\mathbf{E}_i$, $\mathbf{H}_i$, of the electron alone, (1) becomes

$$\int\int\int \left(\mathbf{E}_0 + \frac{[\mathbf{uH}_0]}{c} \right) \rho d\tau = -\int\int\int \left(\mathbf{E}_i + \frac{[\mathbf{uH}_i]}{c} \right) \rho d\tau. \qquad (2)$$

If the integral on the right-hand side be worked out, for example, for a case of acceleration in a straight line it gives, as regards the term involving the acceleration, the value

$$\frac{e^2}{6\pi a c^2} \left(1 - \frac{v^2}{c^2} \right)^{-3/2} \frac{dv}{dt},$$

where a is the radius of the electron, and v is the velocity of its center. Thus (1) becomes, to this approximation,

$$\int\int\int \left(\mathbf{E}_0 + \frac{[\mathbf{uH}_0]}{c} \right) \rho d\tau = \frac{e^2}{6\pi a c^2} \left(1 - \frac{v^2}{c^2} \right)^{-3/2} \frac{dv}{dt}. \qquad (3)$$

If one should call the left-hand side of (3) the "external force," and the scalar product of external force and velocity the "rate of doing work (dW/dt), by the external force," he would find

$$\frac{dW}{dt} = \frac{e^2}{6\pi ac^2}\left(1 - \frac{v^2}{c^2}\right)^{-3/2} v\frac{dv}{dt}. \tag{4}$$

On the other hand, the customary expression for the energy of the field of the electron is

$$\frac{1}{2}\int\int\int (\mathbf{E}_i^2 + \mathbf{H}_i^2)dT$$

and this, when worked out, gives

$$\frac{\partial}{\partial t}\int\int\int\left(\frac{\mathbf{E}_i^2 + \mathbf{H}_i^2}{2}\right)d\tau = \frac{e^2}{6\pi ac^2}\left(1 - \frac{v^2}{c^2}\right)^{-3/2} v\frac{dv}{dt} + \frac{e^2}{24\pi ac^2}\left(1 - \frac{v^2}{c^2}\right)^{-1/2} v\frac{dv}{dt}, \tag{5}$$

which differs from the value in (4) by

$$\frac{e^2}{24\pi ac^2}\left(1 - \frac{v^2}{c^2}\right)^{-1/2} v\frac{dv}{dt}.$$

The difference has nothing to do with neglect of the Poynting flux term connected with the rate of increase of energy, nor with the terms involving derivatives higher than the second, which are neglected in (3). The discrepancy is, in fact, of the same order of magnitude as the whole quantity concerned; and, as may be seen by neglecting v^2/c^2, it is equivalent to a change of the rest mass in (3) from $e^2/6\pi ac^2$ to

$$\frac{e^2}{6\pi ac^2} + \frac{e^2}{24\pi ac^2} = \frac{5}{24}\frac{e^2}{\pi ac^2}.$$

In order to avoid the difficulty, Poincaré [1] has even gone so far as to invent forces of non-electrical origin in the electron to account for the discrepancy.

The present writer has shown that if a proper interpreta-

[1] Poincaré, "Sur la dynamique de l'électron," *Rendiconti del Circolo Mathematico di Palermo*, 21, p. 129, 1906.

tion of the significance of the equations is made,[2] there is no discrepancy whatever. The questions involved are purely algebraic and in any ultimate discrepancy, would involve a violation of the "conservation of algebra" rather than the conservation of energy. The point involved is that the fundamental energy equation in electrodynamics arises from the algebraic consequence of the electromagnetic equations to the effect that,

$$\iiint \left(\mathbf{u} \cdot \overline{\mathbf{E} + \frac{[\mathbf{uH}]}{c}} \right) \rho d\tau = -\frac{\partial}{\partial t} \iiint \left(\frac{\mathbf{E}^2 + \mathbf{H}^2}{2} \right) d\tau - c \iint [\mathbf{EH}]_n dS. \quad (6)$$

This relation is true for any field or portion of a field which in itself forms a solution of the electromagnetic equations. It is, therefore, true of the field $\mathbf{E}_i$, $\mathbf{H}_i$, of the electrons alone, so that

$$\iiint \left(\mathbf{u} \cdot \overline{\mathbf{E}_i + \frac{[\mathbf{uH}_i]}{c}} \right) \rho d\tau = -\frac{\partial}{\partial t} \iiint \left(\frac{\mathbf{E}_i^2 + \mathbf{H}_i^2}{2} \right) d\tau - c \iint [\mathbf{E}_i \mathbf{H}_i]_n dS, \quad (7)$$

writing $\mathbf{u} \equiv \mathbf{v} + \Delta\mathbf{v}$, where $\mathbf{v}$ is the velocity of the center of the electron, and then utilizing (2), equation (7) becomes

$$v \iiint \left(\mathbf{E}_0 + \frac{[\mathbf{uH}_0]}{c} \right) \rho d\tau = \iiint \left(\Delta\mathbf{v} \cdot \overline{\mathbf{E}_i + \frac{[\mathbf{uH}_i]}{c}} \right) \rho d\tau + \frac{\partial}{\partial t} \iiint \left(\frac{\mathbf{E}_i^2 + \mathbf{H}_i^2}{2} \right) d\tau + c \iint [\mathbf{E}_i \mathbf{H}_i]_n dS. \quad (8)$$

The first integral on the right-hand side of (8) is the one which seems to be lost sight of occasionally in discussions of this matter, and its presence shows that if the left-hand side of (8) is to be called rate of doing work, then the second term on the right-hand side is not appropriate to the title, rate of in-

[2] W. F. G. Swann, "The Fundamentals of Electrodynamics," *Bulletin of the National Research Council*, No. 24, pp. 41–44, 1922.

crease of energy. If the first term on the right-hand side be worked out, it gives, to the necessary approximations,

$$\frac{-e^2}{24\pi ac^2}\left(1-\frac{v^2}{c^2}\right)^{-1/2} v\frac{dv}{dt},$$

which just cancels the corresponding term in (5) arising out of the second integral on the right-hand side of (8), and thus we are left with perfect consistency all around, and in particular with the result obtained by multiplying both sides of (3) by v as a result perfectly consistent with (5).

While, therefore, there is, and must of necessity be, consistency in the matter, there does remain the first term on the right-hand side of (8), which term "spoils" the meaning of $(\mathbf{E}_i^2 + \mathbf{H}_i^2)/2$ as energy per unit volume of the field. The main object of the present paper is to show that by suitably modifying the equation of motion (1), it is possible to formulate a scheme consistent with the facts, and with the retention of $(\mathbf{E}^2 + \mathbf{H}^2)/2$ as energy per unit volume, unspoiled by the presence of the first term on the right-hand side of (8). At least it is possible to do this by the neglect of terms of small order of magnitude which are, as a rule, negligible.

In the first place, expression (1) is not invariant under the restricted theory of relativity, and while this is not the origin of the trouble which it is the object of this paper to discuss, we shall first recall that Leigh Page [3] has generalized the assumption of Lorentz to a form at least relativistically invariant. According to the assumption of Leigh Page, there exists a set of axes in relation to which the electron is a sphere, all of whose parts are momentarily at rest, and in this set of axes it moves in such a way that

$$\int\int\int \mathbf{E}'\rho' d\tau' = 0, \tag{9}$$

where we have used dashed letters to denote the quantities in the system of axes concerned, which system we shall call S'. In S', of course, $u' = 0$ everywhere on account of the postulate made. From (9) it is, of course, possible to work out the

[3] Leigh Page, "Is a Mass Retarded by the Reaction of Its Own Radiation?" *Physical Revue*, vol. xi, p. 377, 1918.

motion in any system of axes by utilization of the relativity transformations, and this Page does. However, for our present paper, we desire a rather different picture of the matter. If $k \equiv (1 - q^2/c^2)^{-1/2}$, where q is the resultant velocity of the electron, it is known that $k(\mathbf{E} + [\mathbf{uH}]/c)$, $ki(\mathbf{E}\cdot\mathbf{u})/c$ constitute a 4-vector. Hence

$$k(E_x+[\mathbf{uH}]_x/c) = \beta k'(E_x'+[\mathbf{u'H'}]_x/c)+\beta k'v(\mathbf{E'}\cdot\mathbf{u'})/c^2 \qquad (10)$$

where the x, y, z, t, system S is one defined by

$$x = \beta(x' + vt'); \qquad y = y', \qquad z = z', \qquad t = \beta\left(t' + \frac{v}{c^2}x'\right)$$

and is one in which S' has a velocity v parallel to the axis of x. The quantity β is, of course,

$$\beta \equiv (1 - v^2/c^2)^{-1/2}.$$

Since u' is everywhere zero in S', (10) gives

$$k(E_x + [\mathbf{uH}]_x/c) = \beta k' E_x'. \qquad (11)$$

Now ku, kic constitute a 4-vector, so that

$$k = \beta(k' + v/c^2 k' u_x')$$

or, since

$$u_x' = 0,$$

$$k = \beta k'. \qquad (12)$$

Thus (11) gives

$$E_x + [\mathbf{uH}]_x/c = E_x'. \qquad (13)$$

Now $\rho d\tau$ is an invariant. Thus let us multiply (13) by $\rho d\tau$ on the left and $\rho' d\tau'$ on the right and integrate throughout all space at constant t'.

$$\iiint_{t'=\text{const.}} (E_x + [\mathbf{uH}]_x/c)\rho d\tau = \iiint_{t'=\text{const.}} E_x'\rho' d\tau'.$$

For the y and z directions we obtain

$$\iiint_{t'=\text{const.}} (E_y + [\mathbf{uH}]_y/c)\rho d\tau = 1/\beta \iiint_{t'=\text{const.}} E_y'\rho' d\tau'.$$

$$\iiint_{t'=\text{const.}} (E_z + [\mathbf{uH}]_z/c)\rho d\tau = 1/\beta \iiint_{t'=\text{const.}} E_z'\rho' d\tau'.$$

In virtue of the fundamental assumption of Page, the right-hand side of each of these three equations is zero. Hence

$$\int\int\int_{t'=\text{const.}} (\mathbf{E} + [\mathbf{uH}]/c)\rho d\tau = 0. \tag{14}$$

Equation (14) is the equation which replaces the fundamental assumption of Lorentz. It differs from it in being taken at t' = constant rather than at t = constant.

Again, because $k(\mathbf{E} + [\mathbf{uH}]/c)$, $ki(\mathbf{E}\cdot\mathbf{u})/c$ constitutes a 4-vector

$$k(\mathbf{E}\cdot\mathbf{u}) = \beta k'(\mathbf{E}'\cdot\mathbf{u}') + \beta v k'(E_x' + [\mathbf{u}'\mathbf{H}']_x/c),$$

so that using (12), and observing that u' = zero everywhere,

$$(\mathbf{E}\cdot\mathbf{u}) = vE_x'.$$

Multiply by the invariant $\rho d\tau$ and integrate throughout space at constant t'. Then, since

$$\int_{t'=\text{const.}} E_x'\rho' d\tau' = 0,$$

we find

$$\int\int\int_{t'=\text{const.}} (\mathbf{E}\cdot\mathbf{u})\rho d\tau = 0. \tag{15}$$

Since the vector product of $\mathbf{u}$ and $[\mathbf{uH}]/c$ is always zero, we can, if we wish, replace (15) by

$$\int\int\int_{t'=\text{const.}} (\mathbf{u}\cdot\overline{\mathbf{E} + [\mathbf{uH}]/c})\rho d\tau = 0. \tag{16}$$

As a matter of fact, it would have been possible to infer (15) and (16) directly, because the velocity transformation gives

$$ku_x = \beta k'(u_x' + v)$$

$$k = \beta k'(1 + u_x'v/c^2),$$

so that at t' = constant, and with u_x' = 0,

$$u_x = v.$$

Thus u may be taken outside of the integrals [4] in (15) and (16), leaving a result which is merely the equivalent of (14).

However, the assumption of Page does not relieve us of the difficulty discussed earlier. For, again dividing the field into an external part $\mathbf{E}_0$ and an internal part $\mathbf{E}_i$, (15) is the equivalent of

$$0 = \int_{t'=\text{const.}} (\{\mathbf{E}_0 + \mathbf{E}_i\} \cdot u) \rho d\tau,$$

i.e.,

$$\int_{t'=\text{const.}} (\mathbf{E}_i \cdot \mathbf{u}) \rho d\tau = - v \int_{t'=\text{const.}} \mathbf{E}_0 \rho d\tau,$$

since $\mathbf{u}$ can, at will, be written as v and taken outside of the integrals at constant t'. Now let $x' = 0$ be a point in the charge in the system S' at t'. For example, in the case of a symmetrical distribution of charge, let $x' = 0$ be the plane of symmetry. Let the corresponding point have the component value x_0 at $t = t_0$ in S.

Then

$$t' = \beta \left(t_0 - \frac{v}{c^2} x_0 \right).$$

For any other point in S, the corresponding value of t at constant t' is such that

$$t' = \beta \left(t - \frac{v}{c^2} x \right).$$

Hence

$$t = t_0 + \frac{v}{c^2} (x - x_0).$$

Put

$$x - x_0 = \delta x.$$

Then

$$t = t_0 + \frac{v}{c^2} \delta x.$$

---

[4] The axis is chosen momentarily parallel to the velocity u.

Hence

$$\iiint_{t'=\text{const.}} (\mathbf{E}_i \cdot \mathbf{u})\rho d\tau = \iiint_{t=t_0+(v/c^2)\delta x} (\mathbf{E}_i \cdot \mathbf{u})\rho d\tau$$

$$= \iiint_{t=t_0} (\mathbf{E}_i \cdot \mathbf{u})\rho d\tau + \iiint_{t=t_0} \frac{v}{c^2}\delta x \frac{\partial}{\partial t}\{(\mathbf{E}_i \cdot \mathbf{u})\rho d\tau\},$$

where we have discarded time derivatives of order higher than $\frac{dv}{dt}$. Hence

$$\iiint_{t=t_0} (\mathbf{E}_i \cdot \mathbf{u})\rho d\tau = \iiint_{t'=\text{const.}} (\mathbf{E}_i \cdot \mathbf{u})\rho d\tau$$

$$- \frac{v}{c^2}\iiint_{t=t_0} \delta x \frac{\partial}{\partial t}\{(\mathbf{E}_i \cdot \mathbf{u})\rho d\tau\}. \quad (17)$$

Let us now consider

$$I = \iiint_{t=t_0} \delta x \frac{\partial}{\partial t}\{(\mathbf{E}_i \cdot \mathbf{u})\rho d\tau\}. \quad (18)$$

We shall make the customary approximation involved in the quasi stationary principle to the effect that we may consider the system at each instant as obtainable from a stationary system related to it by the relativity transformation. This system S'' is, of course, the same as S' except that the distribution in it corresponds to t = constant rather than t' = constant. Now using two dashes to denote quantities in S'',

$$u = v + \frac{d}{dt}(\delta x''/\beta).$$

Now

$$\frac{\partial u}{\partial t} = \frac{du}{dt} - v\frac{\partial u}{\partial x}. \quad (19)$$

In view of the occurrence of v/c^2 outside the last integral in (17), we shall neglect the term in v in (19), and write

$$\frac{\partial u}{\partial t} = \frac{du}{dt}.$$

Hence

$$\frac{\partial u}{\partial t} = \frac{dv}{dt} + \delta x'' \frac{d^2}{dt^2}(1/\beta).$$

The second term in the expression contains terms of the order v/c or lower order, and again in view of the occurrence of v/c^2 outside of the last integral in (17), we shall neglect them. Thus

$$\frac{\partial u}{\partial t} = \frac{dv}{dt}.$$

Now $\rho d\tau$ is invariant for corresponding elements in S and S''. Moreover, the component of $\mathbf{E}_i$ parallel to the velocity is the same in S'' as in S. Also $\delta x = \delta x''/\beta$, so that

$$I = \frac{\dot{v}}{\beta} \int\int\int_{t=t_0} \partial x'' \mathbf{E}_i'' \rho'' d\tau''. \tag{20}$$

The integral is a constant quantity characteristic of the distribution of charge in the system S'' at t = constant and as a matter of fact the integral is the same as

$$\int\int\int_{\text{evaluated at } t' = \text{const.}} \delta x' \mathbf{E}_i' \rho' d\tau'.$$

Thus, for the case of a charge e which exists in the form of a spherical shell of radius a when at rest, the integral has the value $e^2/24\pi a$, where we neglect contributions to the field $\mathbf{E}_i$ involving the acceleration and higher derivatives. In this case

$$I = e^2\dot{v}/24\pi a$$

and equation (17) gives

$$\int\int\int_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau = \int\int\int_{t'=\text{const.}} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau - e^2 v\dot{v}/24\pi a c^2, \tag{21}$$

or, since the vector product of $\mathbf{u}$ and $[\mathbf{uH}]/c$ is zero,

$$\int\int\int_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau = \int\int\int_{t'=\text{const.}} (\mathbf{u}\cdot\overline{\mathbf{E}_i + [\mathbf{uH}_i]/c})\rho d\tau - e^2 v\dot{v}/24\pi a c^2. \tag{22}$$

Taking $\mathbf{u}$ outside the first integral on the right-hand side, since it is constant and equal to v at $t' =$ constant, and further, writing $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_i$ and $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_i$, and using (14), equation (22) becomes

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau = -v \iiint_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau - e^2 v\dot{v}/24\pi a c^2. \quad (23)$$

It is now an algebraical fact that

$$\iiint_{t=\text{const.}} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau = -\frac{\partial}{\partial t}\iiint \left(\frac{\mathbf{E}_i^2 + \mathbf{H}_i^2}{2}\right) d\tau - c\iint [\mathbf{E}_i\mathbf{H}_i]_n dS.$$

Hence,

$$v \iiint_{t'=\text{const.}} \left(\mathbf{E}_0 + \frac{[\mathbf{u}\mathbf{H}_0]}{c}\right)\rho d\tau = \frac{e^2 v\dot{v}}{24\pi a c^2} + \frac{\partial}{\partial t}\iiint \left(\frac{\mathbf{E}_i^2 + \mathbf{H}_i^2}{2}\right) d\tau + c\iint [\mathbf{E}_i\mathbf{H}_i]_n dS \quad (24)$$

and once again we arrive, up to the second order, exclusive, at the same discrepancy as before as regards the rate of doing work by the external force and rate of increase of energy of the field, if we wish to call the left-hand side of (24) the rate of doing work by the external force [5] and $(\mathbf{E}_i^2 + \mathbf{H}_i^2)/2$ the energy per unit volume of the field of the electron.

---

[5] The left-hand side in question may be written

$$v \iiint_{t=t_0+v\delta x/c^2} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau.$$

Now, in general, $\mathbf{E}_0$ and $\mathbf{H}_0$ vary very little over the charges, the situation being quite different from what it is for $\mathbf{E}_i$ and $\mathbf{H}_i$. The addition $v\delta x/c^2$ to t_0, therefore, causes contributions of opposite sign, fore and aft, of the representative point in the charge. In the case of a symmetrical distribution of charge with a representative point at the center of symmetry, and for a field $\mathbf{E}_0$, $\mathbf{H}_0$, uniform over the charge, the contribution made by the term $v\delta x/c^2$ would be zero, and in all cases it is small unless the field varies appreciably over the extent of the charge, or varies appreciably with time in a time comparable with v/c times the time necessary for light to travel a distance comparable with the dimensions of the charge.

In general, in the case of a distribution of charge of arbitrary shape considered as an entity as regards its motion, the integral in (20) assumes a value α, characteristic of the charge distribution in the system referred to axes in which it is at rest, and of the total amount of the charge. Thus, neglecting v^2/c^2.

$$I = \alpha\dot{v}$$

and equation (24) results, with $e^2/24\pi a$ replaced by α.

Suppose, however, that instead of assuming the equation of motion (14), we assume an equation of motion of the form

$$k\int\int\int_{t'=\text{const.}} (\mathbf{E} + [\mathbf{uH}]/c)\rho dT = \frac{\alpha}{c^2}k\frac{d}{dt}(k\mathbf{w}), \qquad (25)$$

where k has the meaning already defined, i.e.,

$$k \equiv (1 - q^2/c^2)^{-1/2},$$

where q is the resultant velocity of the charge, and where $\mathbf{w}$ is really equal to v, but has been momentarily designated by a different symbol, since we wish to emphasize the 4-vector character of

$$k\frac{d}{dt}(k\mathbf{w}), \qquad k\frac{d}{dt}(kic).$$

Equation (25) is now relativistically invariant and neglecting v^2/c^2, we may write it [6]

$$\int\int\int (\mathbf{E} + [\mathbf{uH}]/c)\rho d\tau = \frac{\alpha}{c^2}\dot{v}. \qquad (26)$$

In the step between (22) and (23) we now have, in place of the first term on the right-hand side of (23)

$$-v\int\int\int_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{uH}_0]/c)\rho d\tau + \alpha v\dot{v}/c^2$$

[6] Of course, neglect of v^2/c^2 destroys the strict invariance. However, we pay our homage to the strict invariance by making the equations conform to it. Then, for the sake of showing that our procedure involved in adopting (25) results in at least approximate consistency as regards the points which it is the main object of this paper to discuss, we find it convenient to neglect v^2/c^2.

and the term $e^2v\dot{v}/24\pi ac^2$ in (23) is, of course, replaced by $\alpha v\dot{v}/c^2$, so that the two terms in α cancel, leaving

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau = -v\iiint_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau, \quad (27)$$

which leads to

$$v\iiint_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau = \frac{\partial}{\partial t}\iiint \frac{(\mathbf{E}_i^2 + \mathbf{H}_i^2)}{2} d\tau + c\iint [\mathbf{E}_i\mathbf{H}_i]_n dS. \quad (28)$$

Thus, by the artifice of modifying the fundamental-force equation to the form (25) [7] we can, at any rate up to the second order, preserve the energy equation (28) in its customarily recognized form. Equation (25) is, of course, the equivalent of introducing a material mass whose rest value is α/c^2.

Another aspect is of some interest. We have

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E})\rho d\tau = \iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_i)\rho d\tau + \iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E}_0)\rho d\tau,$$

so that, using (22), but with the last term therein generalized

---

[7] The same end may be reached by replacing (14) by

$$\iiint_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau = -(1+\lambda)\iiint_{t'=\text{const.}} (\mathbf{E}_i + [\mathbf{u}\mathbf{H}_i]/c)\rho d\tau.$$

In the step between (22) and (23), we now have, in place of the first term, on the right-hand side of (23),

$$-v\iiint_{t'=\text{const.}} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau - \lambda v\iiint_{t'=\text{const.}} (\mathbf{E}_i + [\mathbf{u}\mathbf{H}_i]/c)\rho d\tau.$$

The second integral in this expression works out to $-e^2/6\pi ac^2$ in the case of a Lorentzian electron, and is, in general, of the form $-\gamma\dot{v}$, so that if we chose λ so that

$$\lambda\gamma = \alpha/c^2,$$

remembering that the last term in (23) is in the general case $-\alpha v\dot{v}/c^2$, we see that (23) leads to (27), and the desired end is secured.

to the form $-\alpha v i/c^2$, we have

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E})\rho d\tau = \iiint_{t'=\text{const.}} (\mathbf{u}\cdot\mathbf{E}_i + [\mathbf{u}\mathbf{H}_i]/c)\rho d\tau - \alpha v\dot{v}/c^2 + \iiint_{t=t_0} (\mathbf{u}\cdot\overline{\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c})\rho d\tau.$$

Since u = constant at t' = constant.

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E})\rho d\tau = v\iiint_{t'=\text{const.}} (\mathbf{E}_i + [\mathbf{u}\mathbf{H}_i]/c)\rho d\tau - \alpha v\dot{v}/c^2 + v\iiint_{t=t_0} (\mathbf{E}_0 + [\mathbf{u}\mathbf{H}_0]/c)\rho d\tau.$$

Now, to the extent that we may, as already discussed, evaluate the last integral at t' = constant instead of at $t = t_0$ = constant, we may write

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E})\rho d\tau = v\iiint_{t'=\text{const.}} (\mathbf{E} + [\mathbf{u}\mathbf{H}]/c)\rho d\tau - \alpha v\dot{v}/c^2.$$

If, therefore, we assume (26), the right-hand side of the above equation, is zero, and there results

$$\iiint_{t=t_0} (\mathbf{u}\cdot\mathbf{E})\rho d\tau = 0 \tag{29}$$

or, if we prefer,

$$\iiint_{t=t_0} (\mathbf{u}\cdot\overline{\mathbf{E} + [\mathbf{u}\mathbf{H}]}/c)\rho d\tau = 0. \tag{30}$$

Since it is an algebraical fact that the left-hand side of (30) is always equal to

$$-\frac{\partial}{\partial t}\iiint \frac{(\mathbf{E}^2 + \mathbf{H}^2)}{2}/d\tau - c\iint [\mathbf{E}\mathbf{H}]_n dS$$

we have

$$\frac{\partial}{\partial t}\iiint \frac{(\mathbf{E}^2 + \mathbf{H}^2)}{2} d\tau = -c\iint [\mathbf{E}\mathbf{H}]_n dS. \tag{31}$$

A statement which implies that the time rate of change of the electromagnetic energy as ordinarily understood within a

region is equal to the total inward Poynting flux through the boundary of the region, regardless of the presence of charges within the region. However, the truth of the law involves

(1) The modification of the force equation along the lines we have suggested.

(2) The neglect of the higher-order terms which we have referred to.

(3) The condition that the "external field" associated with any charge shall not vary appreciably over the charge, and shall not vary appreciably with time during a time equal to v/c times the time taken for light to travel a distance comparable with the dimensions of the charge.

It is, of course, possible to have a condition that a charge moves in such a way that

$$\int\int\int (\mathbf{E}\cdot\mathbf{u})\rho d\tau = 0$$

regardless of the above requirements, and without the complications and approximations we have discussed, provided that we are willing to forego the requirements of the restricted theory of relativity. The assumption is the practical equivalent, in large part, of an alteration of the rest mass by a numerical factor, as already pointed out.

Finally, it may be remarked, that since the term which causes all the trouble (i.e., the term represented by the first integral on the right-hand side of (8) or its equivalent in the later discussions) is the same order of magnitude as

$$\frac{\partial}{\partial t}\int\int\int \left(\frac{\mathbf{E}^2 + \mathbf{H}^2}{2}\right) d\tau$$

its complete neglect does not alter the truth of (31) as regards order of magnitude.

The main reason for writing the foregoing paper on this rather time-worn subject is the necessity of crystallizing the subject for the purpose of another paper on "Electrodynamics and the Mutual Annihilation of Positive and Negative Electricity." [8]

[8] This paper follows the present one in an early issue of the JOURNAL OF THE FRANKLIN INSTITUTE.

CRYSTAL STRUCTURE AND ATOMIC PROPERTIES OF ALLOYS CONTAINING TRANSITION ELEMENTS.*

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THE TRANSITION ELEMENTS.

According to Bohr, more than half the number of metallic elements belong to series within which a gradual consolidation of the inner electron groups of the atoms takes place. These metals—the so-called transition elements—consist of the series 21Sc-28Ni, 39Y-46Pd, 57La-78Pt, 89Ac-92U. Bohr has marked them out by enclosing them in frames in his periodic table (Fig. 1).

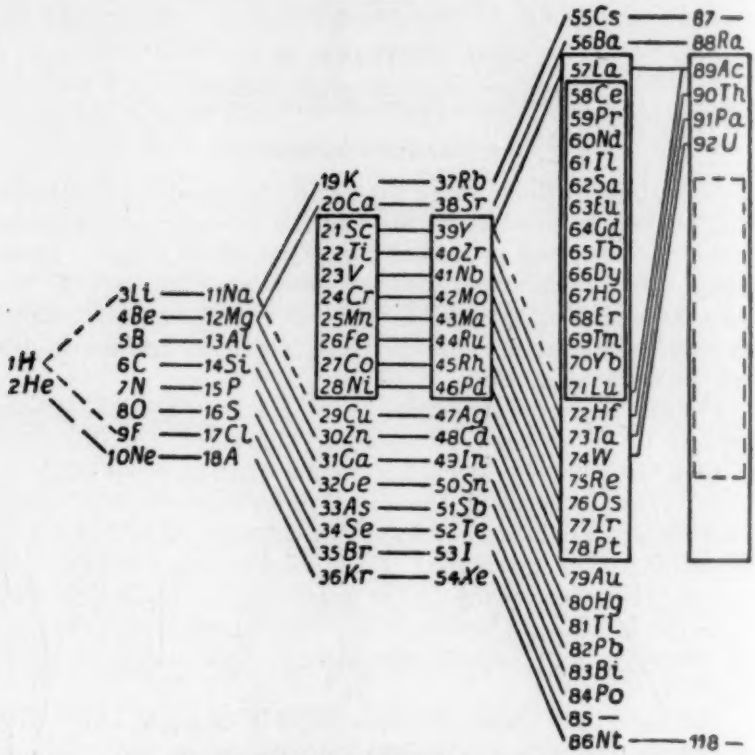
The electronic configuration of the atoms of these elements seems to be of an easily changeable character, i.e. the steps between their energy levels are smaller than in other kinds of atoms. Because of this, their ions differ from those of other elements inasmuch as they have the capacity of absorbing in the visible part of spectrum. Their solutions are consequently colored. Further, owing to the assymetry of their ions they are in the ionic state generally not diamagnetic, like the normal elements, but instead are more or less distinctly paramagnetic.

The fact that these elements exhibit variable valency is apparently connected with the peculiarity in their atomic structure. But, as we know, they are not unique in this respect. Apart from their pronounced catalytic effect nothing has so far been discovered which might be considered to be generally characteristic of the chemistry of their oxides and salts, i.e. their compounds which up till our days have been the most thoroughly investigated. Only within certain groups of them some conformity in chemical properties has been ascertained. The rare earths resemble each other closely

* Presented at a meeting held Thursday, February 5, 1931.

which, as we know, may be referred to the fact that they belong mainly to an element series in which the successive development of the electronic configuration, with rising atomic number, takes place comparatively deep in the interior of the

FIG. 1.



The periodic table of the elements according to Bohr.

atoms. As pointed out by A. Werner (1) certain general characteristics may be noted regarding the chemical character of elements also within other groups of transition elements, as e.g. those belonging to the Sc-Ni group. This does not imply, however, that they differ sharply from neighboring elements, as, according to Werner, scandium in certain respects resembles the preceding elements potassium and calcium, whereas chromium, manganese, iron, cobalt and nickel in some respects are related to the subsequent metals, copper and zinc.

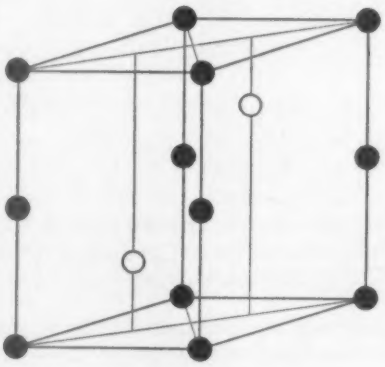
Even if the peculiarity of the transition elements thus does not display itself very distinctly in their reactions, or reaction products, belonging to classical inorganic chemistry, it however—as will be seen in the following—makes itself manifested in a clear way, when they form ingredients of certain compound *metallic* substances.

ALLOYS WITH NICKEL-ARSENIDE STRUCTURE.

When Aminoff and Alsén (2, 3) several years ago determined the atomic grouping of the mineral nickeline, NiAs, they scarcely suspected that it was one of the most generally occurring structure types of the alloy phases that they had encountered. Soon afterwards Alsén (4) also found that pyrrhotite, FeS, as well as breithauptite, NiSb, and the synthetically produced compounds FeSe, NiS, NiSe and CoS all have the same atomic grouping as NiAs. Later V. M. Goldschmidt and his collaborators, however, could add to this list quite a number of other substances, which were all found to have this so-called nickel-arsenide structure (5). All of them are good conductors and have metal lustre so that they may be counted amongst the alloys even though they may contain up to 50 atomic per cent. As, S or Se.

The structure type of nickel arsenide is shown in Fig. 2.

FIG. 2.



● Atom of transition element.

Structure of nickel-arsenide.

The two kinds of atoms are here not structurally equivalent; atoms of the one kind are arranged in a simple hexagonal lattice, while those of the other define a hexagonal close-packed lattice, inserted into the former.

V. M. Goldschmidt has pointed out the following fact in his important papers on the connection between crystal structure and atomic properties (5, 6). All substances which we know for certain to possess the atomic arrangement of nickel-arsenide consist partly of atoms which belong to a transition element, and partly of large, easily polarized atoms, such as those of the elements Sn, As, Sb, Bi, S, Se and Te, the numerical proportion of the two kinds being about equal. The atoms of the first kind always take the position of the points of a simple hexagonal lattice, as seen in Fig. 2.

Sometimes the interstices between the atoms in this structure are so large that a number of excess atoms of the transition element, which are generally comparatively small, may find room there. CuSn [1] (7), FeSb (8), NiBi (9) are phases of this kind, and probably many others which have been proved to be isomorphous with NiAs, but which have not yet been investigated by means of X-ray analysis as to the extension of their homogeneity ranges.

So far, not even all alloys in which crystals with nickel-arsenide structure may be expected, and which may be produced without great difficulty, have been investigated with respect to the occurrence of such phases. During coming years more substances of this kind will certainly be discovered.[2]

From the data already available Goldschmidt has, however, been able to infer that the condition mentioned above is not sufficient for the formation of a nickel-arsenide phase.

[1] Following immediately after the first and third of the series of elements in frames in Bohr's periodic table copper and gold under certain conditions also assume the character of their preceding neighbours, and might in some cases be considered to be transition elements.

[2] Naturally, we must take into consideration that in some systems the phase with nickel-arsenide structure may be stable only at high temperatures. Recently William F. Ehret, e.g., found a phase of this kind also in the Fe-Sn system which is unstable at ordinary temperature, and which is encountered only in alloys which have been quenched from 800° C. A paper on the X-ray analysis of the Fe-Sn system will appear shortly.

It is also necessary that the ratio of the radius of the large atoms to that of the small ones should exceed a certain minimum value. Thus, iron, cobalt, and nickel form phases of the nickel-arsenide type with sulphur and selenium as well as with tellurium. Manganese, however, whose atoms are slightly larger than those of iron, cobalt and nickel, appears to form a nickel-arsenide phase only together with tellurium, and not with sulphur and selenium.

Goldschmidt has thus empirically found certain conditions which seem to apply in the case of the formation of an extensive group of nickel-arsenide phases. The question might be raised, however, if the group mentioned is actually the only one of this kind. If atoms of transition elements are united not with large ones, but instead with very small atoms, such as those of carbon or nitrogen, it may sometimes happen that the metal atoms form a simple hexagonal lattice. As pointed out recently by Gunnar Hägg (10) it is quite possible that the compounds WC and MoN, whose metal atoms are arranged in this simple way, may be counted amongst the phases with nickel-arsenide structure. The diffraction power of the carbon and nitrogen atoms is too small to enable a determination of their relative position. From sundry reasons it seems probable, however, that the metalloid atoms are arranged in the same way as the large atoms in Fig. 2, so that we have to deal with nickel-arsenide structures also in these cases.

That being so, the axial ratio of these crystals would actually be considerably greater than that of the stannides, arsenides, sulphides etc. mentioned, and amount to 1.95, instead of 1.2–1.7. This is, however, easily explained by the fact that the carbon and nitrogen atoms occupy much less room than the atoms of tin, arsenic, sulphur, etc., so that they do not separate the chains formed by the atoms of the transition elements as much as the latter ones. This assumption is upheld by the figures given in Table 1 in which the

TABLE 1.

Axial Ratio of some Series of Nickel-Arsenide Phases.

Phase.	c/a.	Phase.	c/a.	Phase.	c/a.	Phase.	c/a.
FeS.....	1.69	CoS....	1.52	NiS....	1.55	NiAs...	1.39
FeSe....	1.63	CoSe...	1.47	NiSe....	1.46	NiSb...	1.31
FeTe....	1.26	CoTe...	1.38	NiTe...	1.36	NiBi....	1.32

axial ratios c/a of some typical series of NiAs-phases are collected. The axial ratio is here found to decrease with an increasing atom size of the partner combined with the transition element.

The axial ratio will, of course, be specially small if the phase contains more than 50 atomic per cent. of the transition element, i.e. when the interstices of the lattice are to a certain extent filled by excess atoms. Thus, the axial ratio of the nickel-arsenide phases in the copper-tin and in the iron-antimony systems—both holding about 55 atomic per cent. of the transition element—is e.g., only 1.21 and 1.25 respectively.

Naturally, it is of no consequence here, whether compounds like MoN and WC should range amongst the nickel-arsenide phases or not. At any rate, it seems clear that the atomic grouping in question will arise only provided the alloy contains about 50 atomic per cent. of some transition element. Consequently, it may be laid down as a characteristic of these elements that they alone are able to form alloys with this structure.

COMBINATIONS BETWEEN TRANSITION ELEMENTS AND HYDROGEN, BORON, CARBON AND NITROGEN.

Gunnar Hägg has recently analysed the data found in the literature concerning the hydrides, borides, carbides and nitrides of various metals completed with his own experience regarding this kind of substances (11). He found hereby that a combination between a metal and hydrogen, boron, carbon or nitrogen gives rise to products with metallic properties (high conductivity and opaqueness) *only* on the condition that the metal is a transition element.

X-ray investigations by A. E. van Arkel (12), K. Becker and F. Ebert (13) as well as by Hägg have shown that the hydrides, carbides and nitrides of the transition elements may under certain conditions be characterized by very simple atomic arrangements. According to Hägg (11) these will form when the metalloid atoms are sufficiently small (ratio of the atomic radii < 0.59) as compared to those of the metal. Borides which fulfil this stipulation have not yet been investigated by means of X-rays; it is very likely, however, that the

same simple structures will be found here, as those already stated for a great number of products of combinations between transition elements and hydrogen, carbon and nitrogen. The lattice types observed in these substances are the following: the face-centred and body-centred cubic lattices, the hexagonal close-packed one and, as stated above, the simple hexagonal lattice. Sometimes these lattices may be slightly deformed, the cubic one may for instance change into a pseudocubic, face-centred tetragonal lattice, and a slight deformation of the close-packed hexagonal one, may give rise to a pseudohexagonal orthorhombic lattice (14). Owing to the comparatively slight diffraction power of the metalloid atoms, with their few electrons, it is impossible to state the position of these atoms for most phases of this kind. In a few cases it has, however, been possible to perform this determination. Thus, the sodium-chloride structure was encountered in many carbides and nitrides.

The methods applied earlier in inorganic chemistry have offered but an unsatisfactory means of determining which products arise as a result of reactions of transition elements with the metalloids mentioned. The introduction of X-ray methods has however enabled a solving of this question. In spite of this research field still being far from completely investigated, the results obtained so far however clearly show that in this realm of chemistry, where matters earlier appeared to be specially complicated, simple, far-reaching rules are valid.

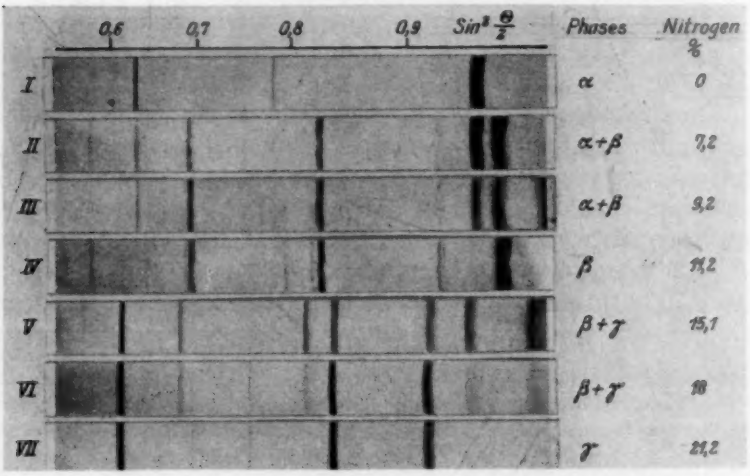
Thus, amongst elements belonging to the Sc-Ni family scandium, titanium and vanadium form carbides with 50 per cent. carbon which all possess sodium-chloride structure. A vanadium carbide, lower in carbon and whose homogeneity range probably corresponds to the composition of the formula V_2C, has been found to have a hexagonal close-packed structure.[3] The atom size of the metals ranging within the iron

[3] In a paper by A. Ôsawa and M. Ôya (*Sci. Rep. Tôhoku Imp. Univ.*, I, 19, 95) the vanadium carbides are given as V_3C and V_4C_3. A comparison between the lattice dimensions of these phases and those of pure vanadium with the corresponding data of other transition elements and their carbides and nitrides, however, shows that the formulæ V_2C and VC are more likely to hold true than those indicated by the Japanese investigators.

family decrease gradually from scandium to nickel. As pointed out by Hägg, the atoms of chromium are too small to be able to form a carbide of sodium-chloride type. Its highest carbide is the orthorhombic Cr_3C_2, then comes a trigonal carbide Cr_7C_3 and finally a cubic phase Cr_4C (15). The highest carbide of manganese appears to be Mn_7C_3 which is isomorphous with the corresponding chromium carbide. Quite recently Einar Öhman has found that manganese and carbon form a compound Mn_4C which is analogous with the chromium carbide Cr_4C, and possibly also a carbide Mn_3C, isomorphous with Fe_3C. As we know, iron only forms the orthorhombic carbide Fe_3C (16). Cobalt and nickel give with carbon the compounds Co_3C and Ni_3C, which are probably isomorphous with Fe_3C. The stability of these carbides decreases in the direction from Fe towards Ni.

If we proceed to the nitrogen compounds the sodium-chloride structure occurs not only in ScN, TiN and VN but it is encountered also in CrN, because of the nitrogen atom being smaller than the carbon atom. According to Ragnar Blix chromium together with nitrogen also forms a close-packed, hexagonal phase, the homogeneity range of which is situated

FIG. 3.



Powder photograms of chromium-nitrogen alloys. Cr.–*K*. radiation. (Ragnar Blix.)

near a composition corresponding to the formula Cr_2N (17). The series of powder photograms of chromium-nitrogen alloys obtained by Blix is reproduced in Fig. 3. The highest nitride of manganese which holds less than 40 atomic per cent. nitrogen, has a pseudo-cubic face-centred tetragonal structure. This metal also forms a nitride with close-packed hexagonal lattice, the homogeneity range of which is situated at about 33 atomic per cent. nitrogen, i.e. corresponding approximately to the composition of the formula Mn_2N, besides also forming a Mn_4N-phase with a face-centred cubic grouping of the metal atoms. The highest iron nitride is the orthorhombic pseudo-hexagonal Fe_2N, whose metal atoms are arranged in a close-packed grouping; then follows a close-packed hexagonal phase, with a homogeneity range which embraces a few atomic per cent. Further, iron also forms a phase Fe_4N which is analogous to the nitride Mn_4N (14). Cobalt and nickel do not seem to form any nitride phases.

TABLE 2.

Survey of Carbides and Nitrides of the Elements belonging to the Scandium—Nickel Series.

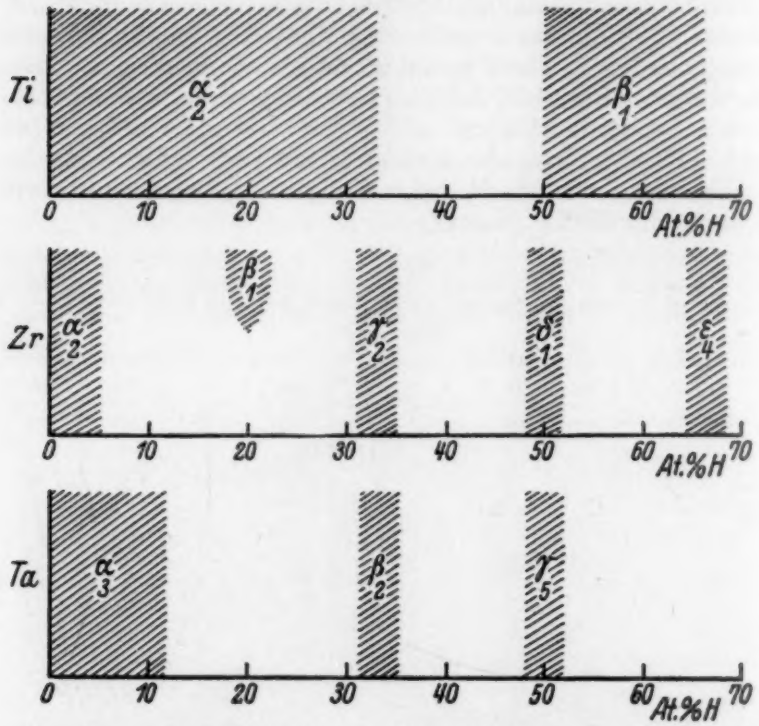
	Sc.	Ti.	V.	Cr.	Mn.	Fe.	Co.	Ni.
Atomic Radius in Å.	1.51.	1.45.	1.33.	1.27.	1.29.	1.26.	1.25.	1.24.
Carbides.....	?	?	V_2C	Cr_4C Cr_7C_3 Cr_3C_2	Mn_4C Mn_3C? Mn_7C_3	Fe_3C	Co_3C	Ni_3C
	ScC	TiC	VC					
Nitrides.....	?	?	?	Cr_2N	Mn_4N Mn_2N Mn_3N_2	Fe_4N Fe_2N	—	—
	ScN	TiN	VN	CrN				

In Table 2 is given a survey of the carbide and nitride phases of the elements belonging to the scandium-nickel series, which contains also the values of the atomic radii of these metals as given by Hägg. As will be seen from this table, the binary systems formed by these transition elements in combination with carbon or nitrogen have already been fairly completely investigated. The alloys of scandium, titanium

and vanadium with low carbon and nitrogen contents however await X-ray analysis. It is very likely that they contain close-packed hexagonal phases, whose composition may correspond to formulæ of the type Sc_2C and Sc_2N.

Quite recently a new report of Gunnar Hägg has been published describing an X-ray analysis of the systems Ti-H, Zr-H and Ta-H (18). As seen from the survey given in this

FIG. 4.



Schematic survey of the phases of the system Ti-H, Zr-H and TaH according to Gunnar Hägg. The figures denote the arrangement of the metal atoms indicating: 1, face-centered cubic; 2, close-packed hexagonal; 3, body-centred cubic; 4, face-centred tetragonal, pseudo-cubic; 5, face-centred orthorhombic, approximately body-centred cubic.

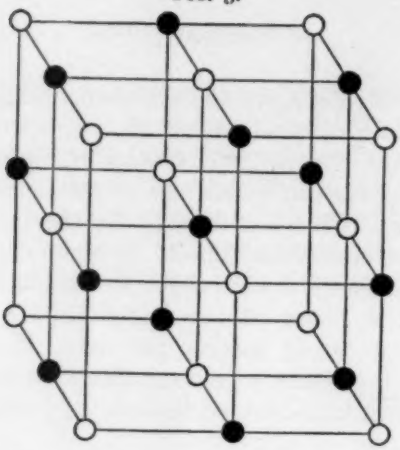
paper which is reproduced in Fig. 4, he has found a phase of close-packed hexagonal structure in each of these systems at a hydrogen concentration of about 33 atomic per cent. In the Ti-H system the homogeneity range of this phase has an

extension from O to exactly the said concentration but in the two others it embraces only a few atomic per cent. about the value mentioned. In the Zr-H system at higher temperature a phase Zr_4H appears in which the metal atoms are arranged in a face-centred cubic lattice. In all these systems phases are also present containing about 50 atomic per cent. H, in which the metal atoms are arranged in the same way. In the Ti-H system the phase of the latter kind is homogeneous within the range 50–67 atomic per cent. H. In the Zr-H system a phase is present with a composition corresponding to ZrH_2, which has a face-centred tetragonal pseudo-cubic structure $\left(\frac{c}{a} = 0.894\right)$.

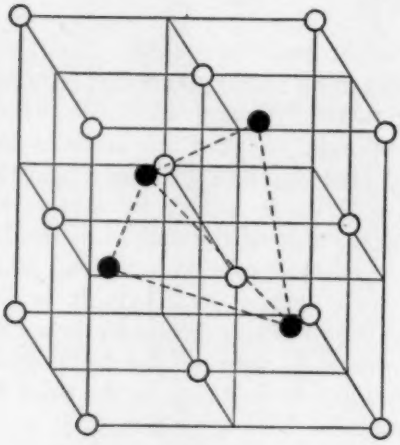
It seems close at hand to assume that the Ti-H and the Zr-H phases containing about 50 atomic per cent. H are structurally analogous to TiC and CrN, i.e. that their atomic grouping corresponds to that of sodium-chloride. If we assume this and also that the hydrogen and the metal atoms are in contact with each other, we arrive, however, at an unreasonably high value of the radius of the hydrogen atom, viz. at 0.7–0.8 Å. instead of about 0.4 Å., which might have been expected. According to Hägg, it is therefore highly improbable that the hydrogen atoms in these cases are situated in the biggest interstices between the metal atoms. It is more likely that they have their place in the next biggest ones, so that the structure of TiH and ZrH does not correspond to that of sodium-chloride (Fig. 5*a*) but instead to that of zincblende (Fig. 5*b*). If TiH has a structure of this kind, the homogeneity range of this phase from 50 to 67 atomic per cent. is also easily explained. The zincblende represents only an intermediate stage in the successive filling up of the next biggest interstices of the close-packed cubic lattice. The complete structure of this kind corresponds to the atomic grouping of fluorite (Fig. 5*c*).

It is natural to suppose also that in the phases in which the metal atoms are arranged in a close-packed hexagonal grouping the hydrogen atoms are situated in the next biggest interstices so that the phases which might be called Ti_2H, Zr_2H and Ta_2H in fact have an incomplete wurtzite structure. Calculating the radius of the hydrogen atoms on the assump-

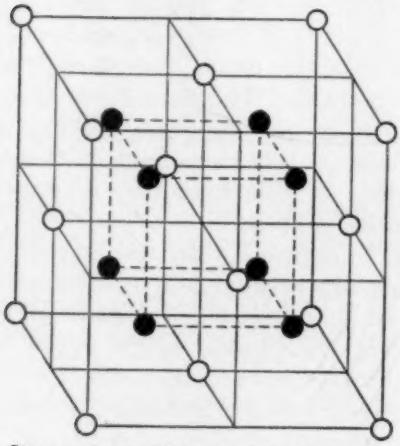
FIG. 5.



c-fluorite.



b. zincblende.



a. sodium-chloride.

Structure types with face centred cubic lattice.

tion that there is contact between hydrogen and metal atoms Hägg has arrived at the figures given in Table 3, in which he has also included the values derived in the same way from the data of Pd_2H and CuH established by J. D. Hanawalt (19) and H. Müller and J. D. Bradley (20).

TABLE 3.

Atomic Radius of the Hydrogen Atoms in Hydrides of Transition Elements according to G. Hägg.

System.	R_H in Å. at 33 Atomic Per Cent. H.	R_H in Å. at 50 Atomic Per Cent. H.
Ti-H	0.43	0.45
Zr-H	0.46	0.48
Ta-H	0.40	0.45
Pd-H	0.37	—
Cu-H	—	0.45

The figures in the table have been obtained under the assumption that in all these phases except in that of the tantalum-hydrogen system containing about 50 atomic per cent. hydrogen the hydrogen atoms are situated in the next biggest interstices. In the phase corresponding to the formula TaH the hydrogen atoms are supposed to be situated in the biggest holes of the lattice formed by the metal atoms.

In another paper by Hägg (21)—also published quite recently—he has given a tabular survey of all the phases formed by a transition element in combination with hydrogen, nitrogen and carbon so far investigated by means of X-ray analysis which fulfill the condition for the formation of simple structures. His data are reproduced in Table 4. The systems are here arranged according to the value of r, which denotes the ratio of the radii of metalloid to metal atoms. When this value exceeds 0.59 the combinations give rise to complicated structures like those of Fe_3C, Cr_7C_3 Mn_4C and similar carbides. The table has recently been completed by H. Arnfelt with Ta_2C, LaC_2 and UC_2 (the former close-packed hexagonal, the two latter pseudo-cubic, face-centred tetragonal, $c/a = 1.2$).

The structure types are denoted according to the coördination numbers and the symmetry of the atomic arrangement. The first figure gives the coördination number of the metal atoms, *a* means cubic or pseudo-cubic, *b* hexagonal or

pseudo-hexagonal symmetry, and the last figure indicates the degree of coördination between metalloid and metal atoms.

It is of interest to note that the composition of the phases corresponds, or comes close, to formulæ of the kinds M_4X, M_2X, MX and MX_2, where M denotes the metal and X the metalloid. Most of the M_2X substances are of the close-

TABLE 4.

Survey of the Interstitial Phases so far Investigated of Transition Elements in Combination with Hydrogen, Carbon and Nitrogen. (*G. Hägg.*)

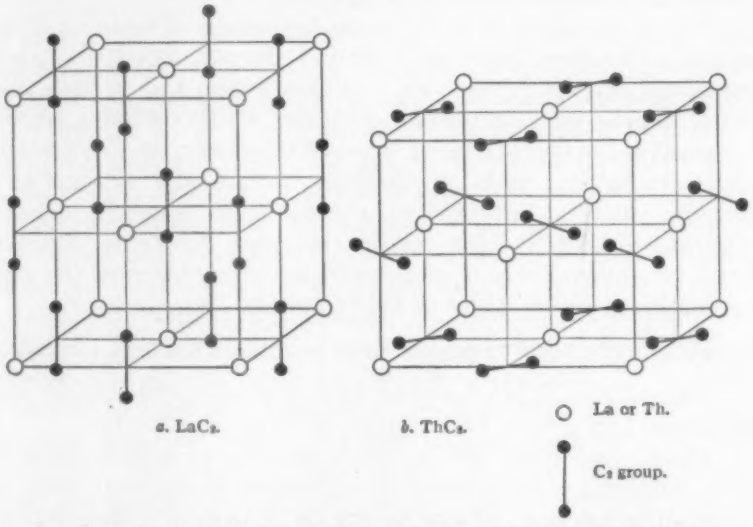
System.	r.	M_4X.	M_2X.	MX.	MX_2.
Zr-H	0.29	12a, 4	12b, 4	12a, 4	ThC_2
Ta-H	0.32	—	12b, 4	8a, 4	?
Ti-H	0.32	—	12b, 4	12a, 4	12a, 4
Pd-H	0.34	—	12a, 4	?	?
La, Ce, Pr, Nd-C	0.42–0.43	?	?	?	LaC_2
Th-C	0.43	?	?	?	ThC_2
Zr-N	0.45	?	?	12a, 6	?
Sc-N	0.47	?	?	12a, 6	?
U-C	0.48	?	?	?	LaC_2
Zr-C	0.48	?	?	12a, 6	?
Nb-N	0.49	?	?	12a, 6	?
Ti-N	0.49	?	?	12a, 6	?
W-N	0.51	—	12a, 6	?	?
Mo-N	0.52	—	12a, 6	8b, 6	?
V-N	0.53	?	?	12a, 6	?
Nb-C	0.53	?	?	12a, 6	?
Ti-C	0.53	?	?	12a, 6	?
Ta-C	0.53	?	12b, 6	12a, 6	?
Mn-N	0.55	12a, 6	12b, 6	?	?
W-C	0.55	—	12b, 6	8b, 6	?
Cr-N	0.56	—	12b, 6	12a, 6	?
Mo-C	0.56	—	12b, 6	?	?
Fe-N	0.56	12a, 6	12b, 6	?	?
V-C	0.58	—	12b, 6	12a, 6	?

packed hexagonal type, and all the MX phases except WC and MoN which are of nickel-arsenide type have their metal atoms arranged in a face-centred cubic lattice. The most important in this connection is, however, that all the phases of these systems so far investigated are of a type which may be termed *interstitial*. In all cases the metal atoms are arranged in a very simple way, and the metalloid atoms are distributed in the interstices between them. When the latter are big enough they are situated in the biggest holes and when they

are too small to come into contact with all the surrounding metal atoms in these places they enter into the next biggest holes.

M. v. Stackelberg (22) has recently communicated a report of an X-ray investigation of some carbides of the type MC_2, where M indicates one of the metals Ca, Sr, Ba, La, Ce, Pr, Nd or Th. He has found here that in all these kinds of crystals the metal atoms are arranged in a face-centred tetragonal lattice, the axial ratio of which differs slightly from 1 (ThC_2: 0.90; the others: 1.14 to 1.18). Pairs of carbon atoms are distributed in the biggest interstices of this lattice, so that structures of deformed sodium-chloride type, shown in Figs. 6*a* and *b*, ensue. Thus, it seems as if even these carbides

FIG. 6.



Crystal structure of dicarbides of transition elements according to M. von Stackelberg.

of the transition elements, La, Ce, Pr, Nd and Th, possessing a high carbon content, would range amongst the above mentioned simply built phases containing this kind of metals in combination with hydrogen, carbon and nitrogen.[4]

[4] It is a striking fact that only transition elements with the very largest atoms are able to form dicarbides, and dinitrides. This evidently stands in a good agreement with the fact mentioned above, and pointed out by Hägg, that the power of these metals to take up carbon and nitrogen increases with an increasing atom size.

A certain relationship between these carbides and those contained in elements with normally formed atoms is certainly to be seen in their isomorphy with CaC_2, SrC_2 and BaC_2. In the reaction with metalloids with small atoms the behaviour of the transition elements however differs widely from that of other metals, inasmuch as they form several different phases, provided their atoms be large enough as compared to those of the other member. These phases are all built up in a simple way, and they are in many cases homogeneous within extended concentration intervals. Other hydrides, carbides and nitrides—as far as they have been subjected to investigation—appear to be homogeneous only at a certain definite composition. As already mentioned, quite a special position amongst the metals must be assigned to the transition elements also because of the fact that their reaction products with hydrogen, carbon and nitrogen are possessed of metallic properties. The dicarbides investigated by von Stackelberg are no exceptions from this rule. As we know, CaC_2, SrC_2 and BaC_2 consist of transparent crystals, while carbides of the rare earths, as corroborated by v. Stackelberg, are electrically well conducting, opaque, besides having the property of metallic lustre. Evidently, a wide and sharply defined difference exists in this respect between hydrides, borides, carbides and nitrides of the transition elements and the corresponding combinations of other metals.

ALLOYS OF TRANSITION ELEMENTS WITH ZINC, CADMIUM AND ALUMINIUM

Among the copper, silver and gold alloy phases certain structure types have been found to recur frequently.

Thus, several phases in this system have a body-centred cubic lattice, i.e. their atoms are grouped in the same way as those of vanadium, of chromium or of α-iron. The various kinds of atoms in these phases may occupy the lattice points in different ways according to the composition, i.e. so-called super-lattices of different kinds may be formed. The fundamental lattice may however be considered as characteristic of crystals of this kind, and it has actually been found that all phases of the copper, silver, and gold alloys which have this structure occur at compositions making the ratio of the number of valency electrons to the number of atoms about 3:2 (23, 24).

In some cases, when according to this rule one might have expected to find a phase with the simple structure mentioned, another structure type, with the complicated atomic arrangement of β-manganese, was encountered instead. Just as manganese differs from its neighbouring elements of the periodic system (V, Cr and α-Fe) in respect to crystal structure, phases like Ag_3Al, Au_3Al and Cu_5Si also form exceptions from the general rule. In spite of the ratio of the number of valency electrons to the number of atoms in these three cases being 3:2, the atoms are not arranged in the same way as in the β-phases of the copper-aluminium and the copper-tin systems (Cu_3Al and Cu_5Sn) but arrange themselves—without forming any super-structure—in the same manner as the atoms in β-manganese (25).

Another important group of structurally analogous phases of the copper, silver- and gold-alloys are the so-called γ-phases which have a structure of the same kind as γ-brass (cubic with 52 atoms in the elementary cube). So far, they have been encountered in all combinations of these metals with zinc, cadmium and mercury with the exception of those of gold and mercury and they have also been found in the systems copper-aluminium and copper-tin. A certain concentration of the valency electrons seems to be necessary for bringing about the atomic grouping of the γ-type too (24–26). The homogeneity ranges of practically all phases of this kind—the single and somewhat doubtful exception being γ-Cu-Hg (27)—includes concentration values which correspond to formulæ of the types Cu_5Zn_8, Cu_9Al_4 and $Cu_{31}Sn_8$. As we see, they all coincide with the ratio of 21 valency electrons to 13 atoms.

Besides the two groups of the β- and the γ-phases, also other kinds of structures recur in the copper-, silver- and gold-alloys. As an example we would cite the compounds $AuZn_3$, $AuCd_3$ and Cu_3Si, recently investigated, which all have the same structure which is pseudo-cubic hexagonal, and also the numerous phases with a close-packed hexagonal structure. The structure types of the β- and the γ-brass however in this connection present the greatest interest as they are represented also in alloys of transition elements together with metals such as zinc, cadmium and aluminium. Thus, FeAl, CoAl and NiAl belong to the β-type. They all have the same structure

as β-brass. It is possible that even MnAl may be included in this group: at least—as found by Elis Persson—a phase (Mn, Cu)Al occurs in the manganese-copper-aluminium alloys in which the manganese and copper atoms in a statistical distribution together form a simple cubic lattice while the aluminium atoms occupy the points of the centering cubic lattice (28).

Ôsawa and Ôgawa have found a phase of the γ-type in the iron-zinc system; they consider its formula to be Fe_3Zn_{10} (29). Walter Ekman has recently corroborated that this phase actually does have γ-structure (30). He thereby also discovered, however, that its homogeneity range at ordinary temperature extends from about 77 atomic per cent. Zn (Fe_3Zn_{10}) to 81 atomic per cent. Zn (Fe_5Zn_{21}). This phase may therefore be indicated as Fe_5Zn_{21} just as likely as Fe_3Zn_{10}.

A closer consideration of the formulæ FeAl, CoAl and NiAl of the β-phases as well as Fe_5Zn_{21} of the γ-phase at once makes clear that the above mentioned rule of formation applies also for this kind of crystals only if the metals iron,cobalt and nickel may be viewed as having a valency of zero.

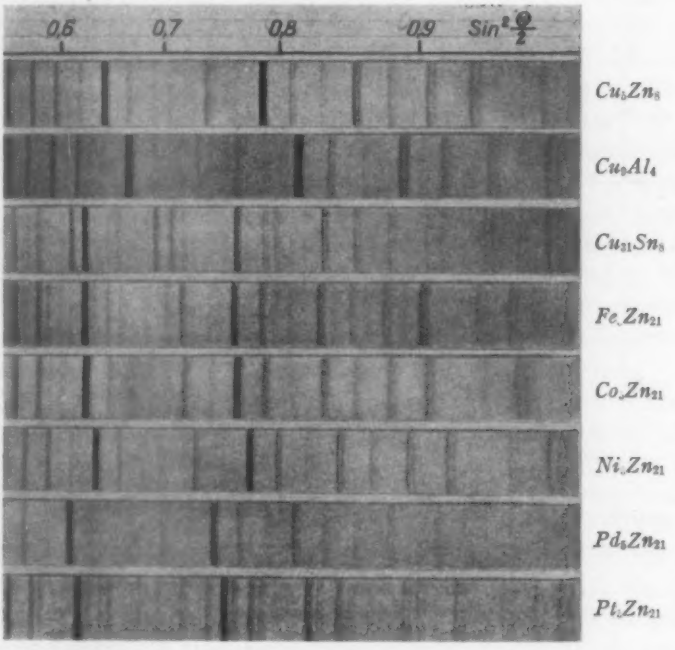
This may appear as a fairly bold assumption; its correctness has however been confirmed by the fact that Ekman in agreement with the rule mentioned succeeded in producing an entire series of alloys with γ-structure. For this purpose he melted transition elements together with zinc and cadmium in proportions according to the formulæ M_5Zn_{21} and M_5Cd_{21}. The X-ray investigation of his products gave as a result that the following had γ-structure: Co-Zn, Ni-Zn, Rh-Zn, Pd-Zn, Pt-Zn and Ni-Cd. Some photograms of them are given in Fig. 7, in which a comparison is made with the X-ray patterns of the corresponding copper-zinc, copper-aluminium and copper-tin phases. The concord of these photograms is striking (31).

In spite of Ekman's investigation of the systems mentioned only having been an orientating one, he has however succeeded in finding a substance which is of further interest for the present problem. As a matter of fact, he struck upon a phase in the cobalt-zinc system which has β-manganese structure, and which must consequently be referred to the same group as the earlier encountered Ag_3Al, Au_3Al and Cu_5Si. It ap-

pears to have a composition corresponding to the formula $CoZn_3$ and, under the presumption of the valency zero for cobalt, the ratio of the number of valency electrons to the number of atoms comes out as 3:2, just as in the cases mentioned above.

The relation between the atomic grouping in the alloys and the average number of valency electrons per atom seem to

FIG. 7.



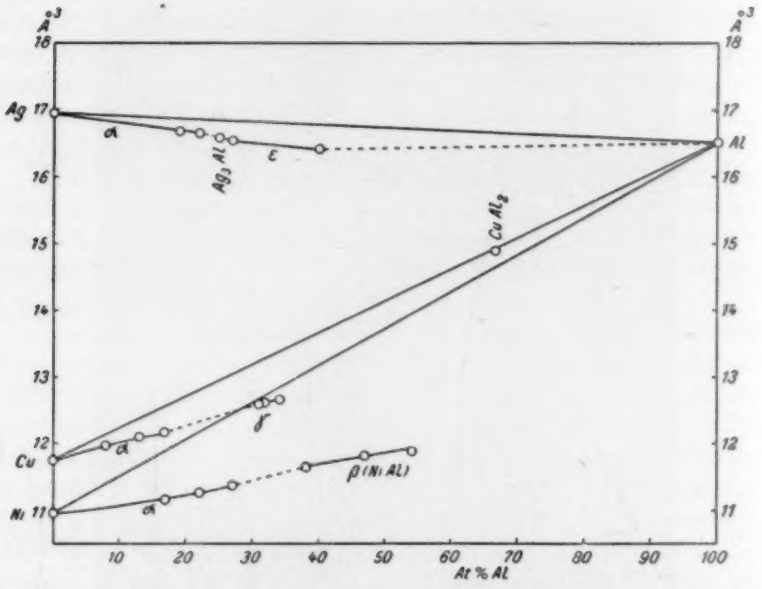
Powder photograms of alloys with γ-brass structure. Fe-K radiation.

indicate that the stability of the crystal structure is in first line dependent on the presence of a number of electrons in the crystal which do not belong to any individual atom but which belong to the lattice as a whole. The character of the remaining part of the atoms appears mainly to be of consequence for the formation of super-structure.

The fact that the transition elements seem to have a valency of zero in the alloys which are structurally analogous

with β- and γ-brass as well as β-manganese implies that in these substances they do not contribute to the common electron group in the lattice. A feature which probably stands in a certain relation to this is the very marked contraction which accompanies the formation of these alloys. Thus, the formation of CoAl and NiAl, for instance, is accompanied by a decrease in volume of the reacting system of no less than

FIG. 8.



Variation of the average volume per atom with composition in the system Cu-Al, Ag-Al and Ni-Al.

about 16 per cent. (32). As seen in Fig. 8 the average volume per atom of the nickel-aluminium system differs much more from that calculated under assumption of additivity than the corresponding quantity of the copper-aluminium and silver-aluminium alloys. As pointed out by Ekman, the γ-phases investigated by him are also formed under a contraction of the reacting system which is quite remarkable. This phenomenon may be explained by the assumption that some of the atoms in these cases keep their electrons more firmly bound than usual. If that is the case, it appears reasonable that they should also occupy less room than usual.

SURVEY AND DISCUSSION.

It is evident from the preceding that the divergence between the transition elements and other metals manifests itself in no less than three different ways in their metallic reaction products.

1. The transition elements alone are able to form phases with *nickel-arsenide* structure (V. M. Goldschmidt).

2. When the transition elements combine with hydrogen, boron, carbon or nitrogen they give rise to reaction products with *metallic* properties, which is not the case with other elements. Provided the atoms of the transition element in a phase of this kind are sufficiently big in relation to those of the metalloid the ensuing structure is of a simple kind, and of a type that may be termed *interstitial* (G. Hägg).

3. In combination with zinc, cadmium or aluminium at certain proportions the transition elements give rise to phases having the same structure as β- or γ-brass. When this happens the relation of the number of valency electrons to the number of atoms in the lattice is the same as that found to be characteristic of the β- or γ-brass phases of the copper-, silver- or gold-alloys, provided the transition elements in these combinations may be considered to have a valency of zero.

We may be entitled to assume that certain relations exist between these phenomenon complexes. Thus, it is striking that the most simple rules are found to apply on the one side when the transition elements are alloyed with elements with large atoms and on the other hand when they unite with metalloids, the atoms of which are very small. It is very probable that the reaction conditions in these two cases stand in a certain connection to each other. Specially if the simple hexagonal lattice of the metal atoms in some carbides and nitrides belong to the crystal structure of the nickel-arsenide type, the analogy in structure of the products may be taken as a proof that the interchange of atoms belonging to transition elements may be the same both with the largest atoms and with the smallest ones.

Thus, even if a certain connection may be traced between the various groups of the experimental results described they however appear at the same time to stand in a certain opposition to each other. Thus, V. M. Goldschmidt holds that the

formation of nickel-arsenide structure does not depend only on the fact that the large atoms are easily polarized but that it may also be referred to the fact that the transition elements give off electrons only with difficulty. The circumstance that they appear as zero-valent when alloyed with aluminium, zinc and cadmium seems to corroborate the correctness of this assumption. Contrary to this, however, stands the fact that phases with nickel-arsenide structure occur even in alloys with copper and gold, which metals have the character of transition elements only in the ionic state.

The only conclusion we can make is consequently that the present experimental results are too incomplete to furnish a coherent idea regarding the conditions prevailing on the scope in question. We may however hope that this will be possible later on, when more experimental data have been compiled.

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CURRENT TOPICS.

"Plaskon," A New Synthetic Resin.—A novel heat-reactive molding compound is now being produced commercially. This new ureabase compound, called "Plaskon," was evolved at Mellon Institute under a series of Industrial Fellowships sustained by the Toledo Scale Company.

"Plaskon" molding compound is said to be easily preformed, and it is pointed out that this property, in conjunction with the high speed of cure, makes possible rapid low-cost mass fabrication by the molder.

Fabricated "Plaskon" is described as unexcelled in color possibilities, combining bright colors with a hard, lustrous surface. Its base shade is one of neutral translucency, permitting pigmenting to give all colors of any intensity, either opaque or translucent. Obviously, as indicated in the publication, infinite variations in mottled or striated effects are possible.

The mechanical and electrical properties of "Plaskon" are said to be excellent; they are summarized in the following table, which has been taken from a research report recently published by Mellon Institute of Industrial Research:

PROPERTIES OF FABRICATED "PLASKON."

Specific gravity	1.43.
Modulus of rupture	10,000 to 14,000 lbs./sq. in.
Tensile strength	4,000 to 6,000 lbs./sq. in.
Compressive strength	25,000 to 30,000 lbs./sq. in.
Impact strength (Sharpe)	0.7 to 1.2 ft. lbs.
Dielectric constant (25° C.)	5 to 6.
Dielectric strength (puncture)	300 to 400 volts per mil.
Water absorption (20° C.; 1/8" section)	0.07 to 0.66 per cent. in 24 hrs.
Resistance to solvents	Unaffected by alcohol, acetone, oil, or other common solvents.
Resistance to acids	Moderately resistant to cold dilute acids. Not resistant to hot or concentrated acids.
Resistance to alkalies	Quite resistant to cold dilute alkalies. Also resists hot, very dilute alkalies, such as soap, borax, cleaners etc.
Hardness (Mohr scale)	3.0 to 3.5.
Hardness (scleroscope)	80 to 95.
Workability	"Plaskon" can be machined, bored, resurfaced, and polished.

METHODS OF HIGH TEMPERATURE TREATMENT.

BY

PAUL P. CIOFFI, A.M.,

Bell Telephone Laboratories,
New York.

INTRODUCTION.

The object of this paper is to describe methods which have been developed in this laboratory for treating metals, chiefly iron and its alloys, at all temperatures up to about 1700° C., considerably above the melting point of iron, and in any atmosphere ranging in pressure from 10^{-8} mm. of mercury to 20 or more atmospheres. The methods of heating, and the forms of the materials heated fall into three rather well-defined groups: (1) Long wires and tapes heated to any temperature up to a few degrees below the melting point by passing currents through them in the presence of a gas (*a*) under a pressure of one atmosphere or less, or (*b*) under a pressure up to 20 atmospheres. (2) Toroids heated by induction in a gas atmosphere, with the gas pressure ranging from 10^{-8} mm. to one atmosphere. (3) Any shape of specimen heated up to about 1700° C. in a molybdenum wound furnace in a gas pressure ranging from 10^{-3} mm. to 20 atmospheres.

In investigations dealing with the effect of heat treatment on the properties of materials, the temperature range covered, often limited by the lack of suitable facilities, is apt to obscure important or interesting effects produced by heat treatments at high temperatures. The new high values of the magnetic permeability of iron recently reported [1] were made possible by employing the methods here described; in fact these methods were all developed in connection with the investigation of the magnetic properties of materials as dependent upon temperature and time of heat treatment and rate of cooling in any atmosphere. These methods are also applicable to other metals which can be shaped into long wires or

[1] P. P. Cioffi, *Nature*, 126, 200–201; Aug. 9, 1930.

tapes or toroids. When short time heat treatments or rapid rates of cooling through certain temperature ranges are desired, the direct heating of straight wires or tapes in any atmosphere by means of a longitudinal current has been found especially advantageous. When heat treatments are to be conducted in very carefully controlled atmospheres or in a high vacuum, the inductive heating of toroidal specimens in glass containers is the most desirable method because by this means it is possible to avoid contamination by foreign substances. Heating of the container is avoided by water cooling. For heat treatments on a larger scale where exceedingly careful control is not particularly necessary it has been found advantageous to use a specially constructed molybdenum wound furnace requiring very little attention in operation over long periods of time. An advantage of this method is that it can be used for heat treating irregularly shaped specimens.

SPECIMENS.

The desired chemical composition of the material, if not directly procurable, was effected by making melts in an Ajax-Northrup high frequency induction furnace. The metal was then cast into rods or plates suitable for working into specimens of the desired shape. The long wire or tape has been found particularly suited for determinations of the effect of time and temperature of heat treatment, chemical composition and mechanical operations on the physical properties of metals, because it lends itself readily to both treatment and physical measurement. On the other hand the toroidal specimen has been found better adapted for determining the effects of various processes on the magnetic properties of magnetic materials because of its freedom from error in magnetic measurements. However, both types of specimens have been advantageously used in this laboratory, the choice-depending upon the nature of the problem. Wire specimens, 60 cm. long, have been used in various diameters ranging from 0.2 mm. to 3 mm., while tape specimens of the same length and 3 mm. wide have been used in various thickness ranging from 0.05 mm. to 1 mm. The toroidal specimens used have an axial height of 6 mm., an outside diameter of 2.85 cm. and an inside diameter ranging from 2.35 cm. to 2.80 cm.

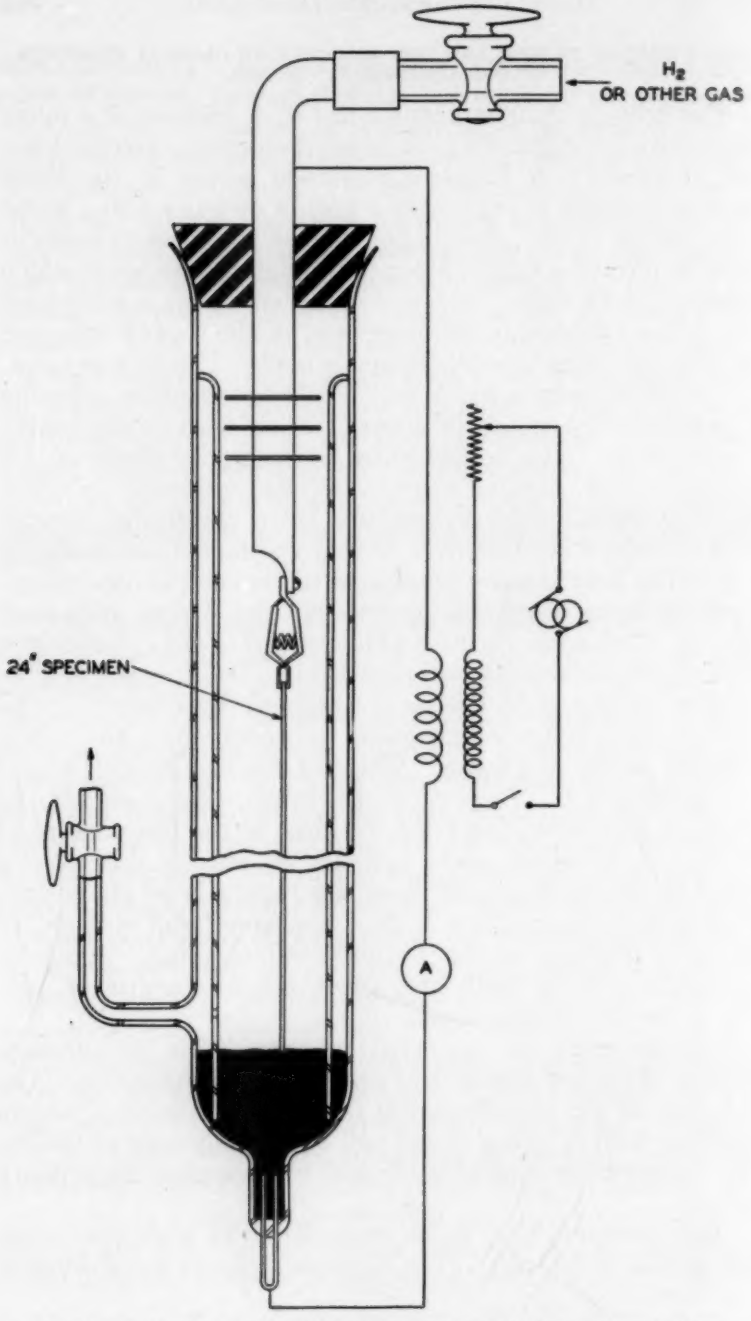
DIRECT HEATING OF WIRE AND TAPE SPECIMENS IN GASES AT PRESSURES OF ONE ATMOSPHERE OR LESS.

The heating chamber, shown in Fig. 1, consists of a pyrex glass tube approximately 5 cm. inside diameter and 90 cm. long, held vertically. A tungsten electrode sealed in the lower closed end makes contact with a pool of mercury filling about 3 cm. of the tube. The upper end of the glass cylinder is flared to receive a rubber stopper through the center of which passes a copper tube. One end of the specimen is suspended from a clip fastened to the lower end of the copper tube and the other end dips into the mercury pool. The mercury contact below permits a quick and flexible connection, allowing the specimen to expand and contract freely without the danger of overstrain. The copper tube is the upper electrode for conducting the heating current to the specimen. Copper flanges soldered to the copper tube below the rubber stopper serve to reduce the quantity of heat conducted and radiated to it. The heat treatment may be carried out in any atmosphere by introducing the gas through the copper tube and allowing it to escape through a tube sealed to the cylinder at a point slightly above the mercury level. The pressure may be adjusted to any point below atmospheric by connecting the exhaust tube to a vacuum pump and controlling the inflow of gas by means of a valve. The pressure is read with a mercury manometer. To prevent disastrous results, should the specimen part when operating too close to the fusion point of the metal, a second glass cylinder of smaller diameter is placed inside the first, resting on the rounded end of the container below the mercury level. The upper end is flared to the inside diameter of the container for centering. A hole in the inside cylinder wall, just above the mercury level, permits a free circulation of gas.

The specimen is connected in series with an ammeter directly to the low side of a 4:1 step-down transformer. The high side of the transformer is connected through a control resistance and switch to a 220 volt alternating current source. The temperature control is effected by changing the primary current.

Temperatures have been measured with a thermocouple and optical pyrometer. The thermocouple, of 2 mil wires of

FIG. 1.



Glass furnace for direct heating of wire or tape specimens in gases at pressures of one atmosphere or less.

Pt, Pt–Rh 10 per cent., is welded to the center of the specimen, the leads being carried out through the top of the glass cylinder along the side of the rubber stopper. A thermocouple of such small size was found to produce no appreciable cooling of the specimen at the point of contact. Since the thermal e.m.f. is read on a potentiometer, the stray alternating current in the thermocouple circuit arising from the potential drop across the point of contact produces no effect on the galvanometer. It is impractical, of course, to weld a thermocouple to each specimen used, but for similar specimens it is only necessary to apply the current-temperature relation determined for one specimen, checking with an optical pyrometer.

When proper corrections have been made for emissivity and window absorption, the temperatures may be measured accurately by means of an optical pyrometer. The advantage of this method is that the temperature may be measured directly for each specimen. However, with temperatures above 1000° C. excessive evaporation of metal to the surface of the glass container makes further visual observation impossible, unless special precautions are taken to avoid the formation of the film at the point of observation. A method of overcoming this difficulty will be described in a later section dealing with the heat treatment of toroidal specimens.

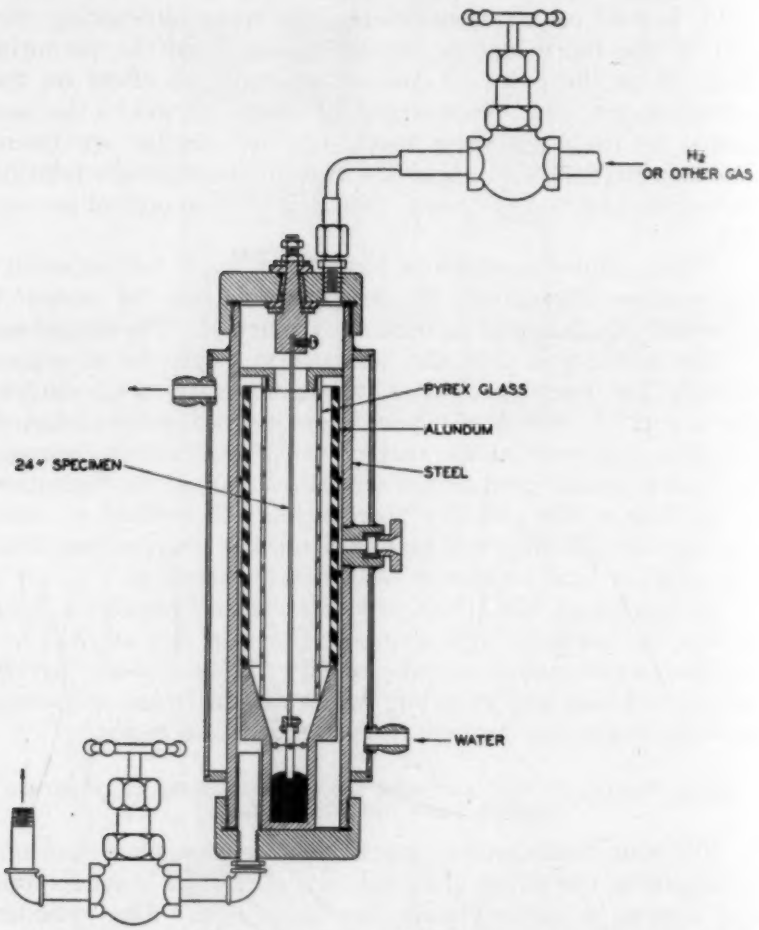
In specimens which have allotropic transformations, such as iron, for instance, at least two points, the α–γ and the γ–δ transformation points may be readily fixed by observing the violent writhing and wriggling which wire and tape specimens undergo in passing through these temperature regions.

DIRECT HEATING OF WIRE AND TAPE SPECIMENS IN GASES AT PRESSURES GREATER THAN ONE ATMOSPHERE.

For heat treatments in gases at pressures higher than one atmosphere, the pyrex glass cylinder described is inadequate and instead a steel cylinder has been used. The cylinder, shown in Fig. 2, is a water-jacketed Shelby steel tube 7.5 cm. outside diameter and 6.25 cm. inside diameter capped at both ends, using copper-asbestos gaskets. The tapered end of one electrode, for electrical connection to the upper end of the specimen, passes through a larger and similarly tapered hole

in the cap, the space in between being filled with litharge and glycerine cement. The electrode is bolted in place, before allowing the cement to set, using several layers of mica washers

FIG. 2.



Steel furnace for direct heating of wire or tape specimens in gases at pressures greater than one atmosphere.

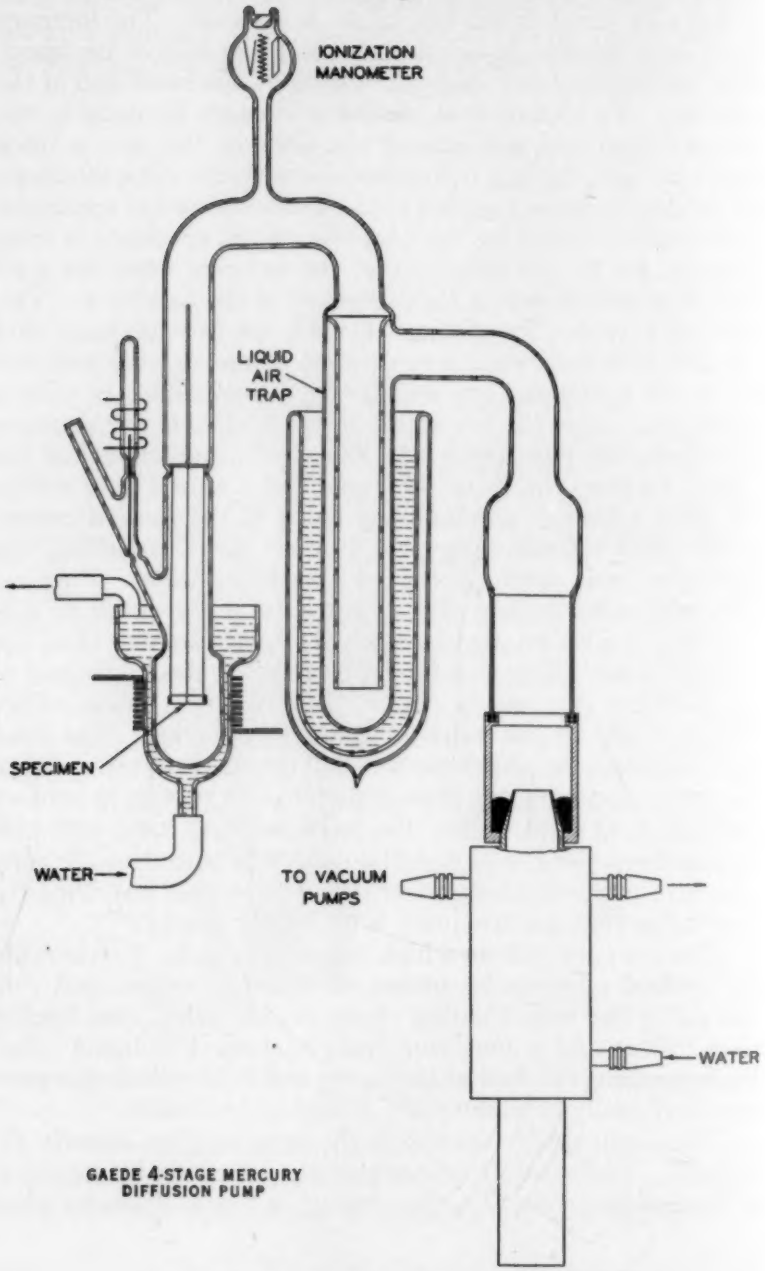
on both sides of the cap for insulation. A set-screw near the lower end of the electrode holds the specimen in position. The upper cap also carries a coupling for connecting to a

source of gas supply. The circulating gas passes out through a steel pipe fitted in one side of the lower cap. The mercury for making flexible connection to the lower end of the specimen, is contained in a steel cup resting on the lower end of the cylinder. To ensure that electrical contact is made in the mercury pool and not against the sides of the cup, a thick steel wire carrying four lighter horizontal guide wires terminating in glass beads is coupled to the lower end of the specimen. The tension exerted by the coupling on the specimen is compensated for by the buoyancy of the mercury when the steel wire sinks into it during the expansion of the specimen. Violent gas currents, circulating between the hot specimen and the cold cylinder, tending to produce a temperature gradient along the specimen, are avoided by surrounding it with a pyrex glass tube, the lower end of which rests in the mercury cup above the mercury level. On the flat upper end of the glass tube rests the flange of a small steel tube fitting within the glass cylinder. This flange, being of the same diameter as the steel cylinder, prevents the hot gas surrounding the specimen from reaching the cold cylinder walls. Furthermore, excessive cooling of the glass tube is prevented by surrounding it with an alundum shield slightly smaller than the steel cylinder. The alundum tube rests on the upper end of the mercury cup and is centered by two thin brass collars fitting snugly to the inside of the steel cylinder. The dead space between the alundum tube and the steel container keeps the gas surrounding the glass cylinder from coming in contact with the cold steel walls. Experiments show that with this arrangement the film of metallic vapor condensed on the glass tube is of uniform density over its entire length, justifying the conclusion that the specimen is uniformly heated.

The gas supply from a high pressure cylinder is reduced to the desired pressure by means of reducing valves, and conducted to the heat treating chamber through 3 mm. Shelby steel tubing and a purifying train contained in heavy steel. By controlling the flow at the outlet and inlet valves, the pressure may easily be maintained at any desired value.

The temperature control is the same as that already described. Temperature measurements are made by means of an optical pyrometer looking through a 6 mm. diameter plate

FIG. 3.



Inductive heating of toroidal specimens in high vacuum.

glass window, 6mm. thick, clamped and sealed at the end of a thick steel tube fitted to the middle of the steel chamber and passing through the water jacket.

INDUCTIVE HEATING OF TOROIDAL SPECIMENS.

For heat treatments in high vacuum or carefully controlled atmospheres, it is necessary to avoid contamination from gases which may be evolved from hot bodies within the heating chamber. This object has been achieved by inductively heating a toroidal specimen in a water-jacketed glass vessel connected either to the source of gas or to a high vacuum pump, as shown in Fig. 3. The specimen is contained in a pyrex glass bulb 7 cm. long and 5 cm. inside diameter. It is suspended from a thin, glass tripod resting on the constriction in the neck of the containing glass vessel, by means of three filaments, 0.1 mm. thick, made of the same material as the specimen. Temperature observations are made through a flat window fused to the end of a tube sealed obliquely to the neck of the bulb. Blackening of the window by metal evaporated from the specimen is prevented by interposing between the two a thin, soft iron sheet, acting as a shutter, partly extending into a flattened, vertical tube sealed to the oblique tube. The shutter is opened by energizing a solenoid around the vertical tube. Water-jacketing prevents the evolution of gas from the walls of the glassware heated by radiation. Water is admitted into the jacket from below and carried off at the top through a tube connected to a water aspirator.

For heat treatments in high vacuum the neck of the bulb is connected to a steel, 4-stage, Gaede, mercury diffusion pump through a liquid air trap, and glass-copper seal. The copper end of the glass-copper seal is soldered to a steel coupling which threads to the high vacuum end of the mercury diffusion pump, the threaded joint being sealed with mercury. The connecting glass tubing is of 3.8 cm. bore and is made as short as possible. Before surrounding the specimen bulb with the water jacket, the glassware is baked to almost the softening point as far back as the liquid air trap.

The source of high frequency alternating current is a portable vacuum tube oscillator of one kilowatt capacity,

energizing a coil of a dozen turns situated on the outside of the water jacket. The temperature of the specimen, read by means of an optical pyrometer, is controlled by changing the high frequency alternating current through the coupling coil by varying the plate voltage of the vacuum tube oscillator. Fine adjustments are made either by changing the degree of coupling between the coil and specimen or by changing the supply voltage. It has been possible in this way to heat-treat magnetic specimens in a vacuum as low as 10^{-8} mm. (read on an ionization manometer, shown in Fig. 3), at temperatures between 1200° C. and 1500° C. for periods as long as 100 hours. Experiments are now under way for melting metals under similar conditions.

The same arrangement has been used to heat-treat metals in controlled atmospheres at pressures up to one atmosphere. The procedure is to admit the gas at a point near the specimen, the desired pressure being maintained by means of the vacuum pumps and an adjustment of the gas inlet valve. For atmospheric pressure the gas is simply allowed to escape at a point somewhat removed from the specimen without operating the pumps. Besides the ionization gauge, a mercury manometer is provided to read pressures up to one atmosphere.

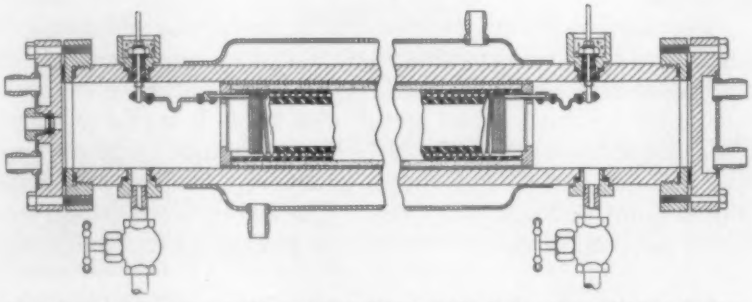
FURNACE TREATMENT.

The methods already described have been found useful not only for preliminary investigations but also where practically ideal conditions were to prevail. Such experiments have since justified the construction of a furnace not only for carrying on experiments on a larger scale, but also for heat treating irregularly shaped specimens. This furnace, consisting of a heating element in a heavy walled steel chamber, has been designed for temperatures up to about 1700° C. and for pressures ranging from vacuum to several atmospheres. A sketch is shown in Fig. 4.

The heating element is contained in a flanged, water-jacketed, Shelby steel tube 10 cm. inside diameter and 14 cm. outside diameter capable of withstanding the pressure developed by the ignition of an explosive mixture of oxygen and hydrogen at an initial pressure of 3 atmospheres. Steel heads, also water-cooled, bolt to the flanges, so that circular knife

ridges protruding from the surface of the heads and flanges, sink into the lead gasket between them, ensuring gas-tight joints. A small, thick, plate glass window in one of the heads serves for visual observations and temperature measurements by means of an optical pyrometer. The electrodes, for making electrical connection to the heating element, are copper rods threaded into isolantite insulators which also thread into steel plugs fitted to opposite ends of the furnace chamber

FIG. 4.



Molybdenum resistance wound furnace and water-jacketed steel container for heat treating irregularly shaped specimens.

beyond the water jacket. Valves for controlling the gas flow through the furnace are also situated at opposite ends of the furnace. As a precaution against leaks all threaded connections are sealed with litharge and glycerine cement.

The heater consists of a threaded alundum tube 5 cm. inside diameter and 90 cm. long wound with two 1.5 mm. diameter molybdenum wires in parallel (0.65 cm. pitch) over 60 cm. of its length. The unthreaded portion of the alundum core at each end is covered with a molybdenum sleeve 0.5 mm. thick and 2.5 cm. long to which is bound a molybdenum rod 5 mm. in diameter. Each end of the winding is fastened to a rod by passing the two parallel strands through separate holes in the nearest end of the rod and then twisting them together. The alundum core makes a snug fit into a slightly shorter alundum shield, and the two are centrally supported within a thin steel cylinder by the bare protruding ends of the inner core which rest in openings in ends affixed to this cylinder. The current terminals are insulated with silica tubing and project beyond the ends of this same thin steel cylinder. The

space between it and the alundum shield is packed with 600 mesh alundum for heat insulation. This assembly makes a snug fit into the heavy steel container already described, the current terminals being connected by means of copper braiding to the heavy copper electrodes at the ends of the furnace chamber.

Temperature control is effected by means of a voltage regulator, consisting of a variable ratio autotransformer for varying the supply voltage from 2.2 to 220 volts in steps of 2.2 volts.

For treatments in various atmospheres, the gas supply is similar to that already described. For vacuum treatments, the powdered alundum packing in the heating element is ordinarily omitted. The metal inlet valve is replaced with a glass stopcock connected with high pressure rubber hose. The exhaust valve and coupling are replaced with a glass-copper joint of large diameter. The latter is connected to a liquid air trap beyond which is the 4-stage mercury diffusion pump.

The methods of heat treatment here described have been developed particularly for heat treating iron in vacuum and in hydrogen, and have operated satisfactorily over a period of years.

I wish to express my indebtedness to Mr. H. W. Weinhart of these Laboratories for important contributions to the design of apparatus here described.

PSYCHO-TECHNICAL DETERMINATION OF THE ECONOMICAL OPTIMUM IN THE ILLUMINATION OF TEXTILE MILLS.

BY

DR.-ING. N. GOLDSTERN AND DR.-ING. F. PUTNOKY.

TRANSLATED BY

ALFRED A. WOHLAUER,

Osram, G.m.b.H. Kommanditgesellschaft, Berlin.

The influence of improved illumination upon the efficiency of human labor and industrial productivity and the economy effected thereby in the cost of production has been definitely established. It yet remains to determine the most favorable illumination or the economical optimum pertaining to different classes of industrial activity.

For this reason a board was formed in Germany about 2 years ago, jointly by the Department of Psycho-Technics (Technical College Berlin) and the Department of "Lichtwirtschaft" of the Osram-Co. Berlin, to carry out a series of experiments to accomplish this purpose.

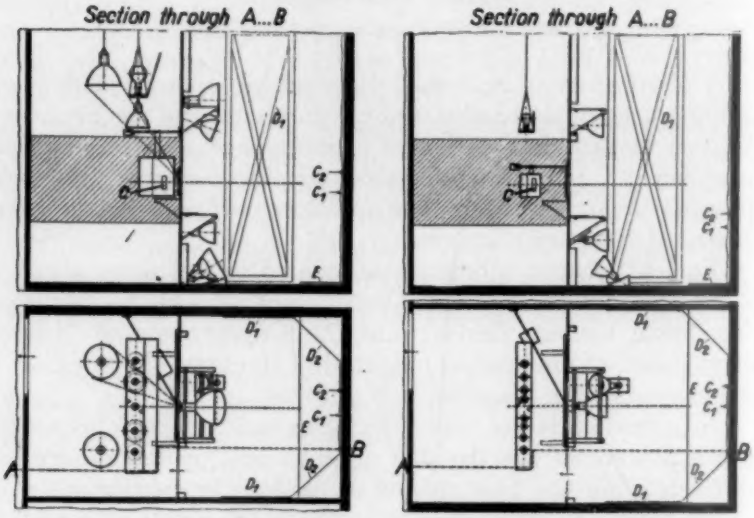
As a first start the textile industry was selected for study and a procedure was decided upon to find by laboratory experimentation the best means of raising the productivity in textile work and consequently to check the resulting methods as to their practical value by applying them to factory work under actual operating conditions.

Preparatory to this work a number of factories were visited in order to get an insight into the existing working conditions and to analyse the work of the weavers with regard to the sential aspects in illumination. It thus was found that the chief components in the work of the weavers involve the recognition of the threads and their defects and that therefore the main factors in illumination would be (of course, aside from glare) the degree of brightness (illumination), contrast, and umbrageousness.

Consequently, a working model was devised in order to

analyse by laboratory experiments the various steps of the weavers under different conditions of illumination and to arrive at an idea of the influence brightness, contrast, and umbrageousness exert upon the perceptibility of the threads and their defects. The experiments were carried out during the time from 9 A.M. to 6 P.M. by students and other technical men, the suitability of whom was established by acuity tests. All necessary precautions were taken to eliminate any errors due to fatigue or excessive temperature changes.

FIG. 1.



Laboratory set-up.
C_3 black curtain.
D_1 black lids.
C_2 and D_2 white surface.

As shown in Fig. 1 the laboratory set-up consisted of 2 chambers (used alternately), each having a partition in the center with a square hole of about 4″ x 4″ for the reception of the working model. The partition was necessary in order to illuminate the model and background independently of each other. With this set-up it was possible to vary the brightness, contrast, and umbrageousness within wide margins. The brightness was changed in a geometrical progression within the range of 0.01 . . . 100 ml. The backgrounds could be

changed from black (coefficient of reflexion 3.3 per cent. into white (79.5 per cent.) by reversing the lids C_1 and D_1 to C_2 and D_2. The diffused illumination of this background was produced by 2 reflectors arranged vertically above each other and the intensity of illumination was changed by using lamps of different sizes therein. This arrangement was chosen, particularly the oblique lids D_1 and D_2, in order to obtain a uniform illumination for binocular vision within a minimum of space. As photometer the Macbeth Illuminometer was used.

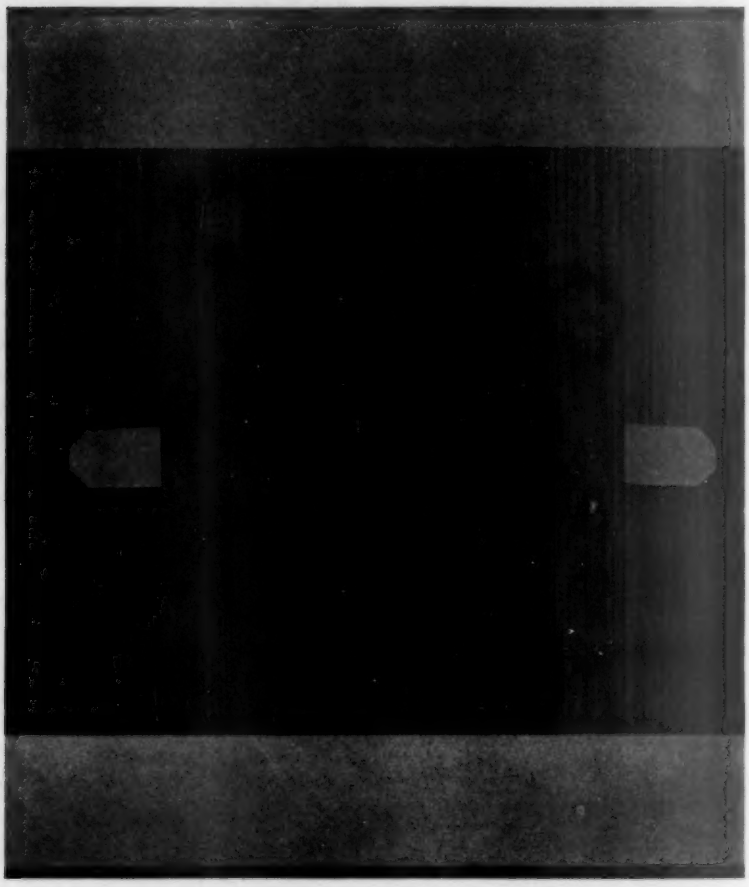
The space in front of the partition representing the work room was equipped for 3 methods of illumination of different intensities. "Normal" illumination meaning the illumination that is usually employed in textile mills was furnished by 2 enamel bowl reflectors which were equipped successively with lamps of different sizes. The indirect illumination was furnished by a horizontal board suspended from the ceiling and lined on the upper side with bare lamps. The third type of illumination which was to serve the purpose of testing the influence of the umbrageousness by casting shadows on the threads of the working model, was produced by a single lamp within a box having a narrow slot, c, thus acting like a point source of light. The intensity of illumination of all 3 classes could be regulated so as to furnish the same steps of brightness on the working model as on the background.

The working model taking the place of the loom, consisted of a wooden frame over which threads of raw cotton were wound in one uniform layer. The diameter of the threads was measured microscopically and found to average 0.071", the distance between the threads being of the same order. The actual testing area placed in front of the opening of the partition measured about 3" x 4" and contained 300 threads marked off by paper marks as illustrated in Fig. 2.

The experiments were carried out in such a manner that each observer seated himself in front of the working model and chose his own most favorable distance therefrom, looking straight at right angle at the threads. For each experiment he was allowed 5 minutes for adaptation to the brightness of the working plane. He had the task to count the 300 threads as quickly as possible, calling out "10" every time 10 threads had been counted. Each call was recorded with the aid of a

stop watch and when 300 threads were counted, the total time of counting was taken and recorded also. If this total time did not agree with the multiple of calls within a range of ± 30 threads, the experiment was repeated. But such inexactness

FIG. 2.



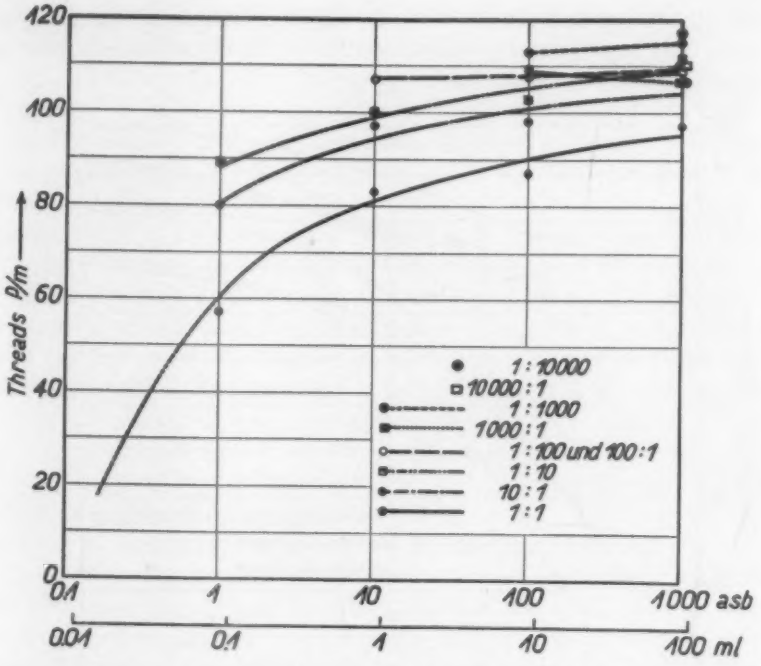
Contrast 100 : 1.
One sample of working model.

was seldom found, except at the lowest intensity of illumination. On the other hand some of the observers acquired a certain training in counting, for instance by taking 2 and

even up to 4 threads together instead of counting each separately. In order to eliminate the influence of such practice which might obscure the results, the sequence of the individual tests at different illumination intensities was changed or else the cyclic rotation of the variations was reversed. In any event, the total time of counting was checked carefully against the time of the individual counts of 10 threads and a correction was applied eventually, if necessary.

The results of the 15 observers were averaged and divided by the number of threads, thus getting the number of threads per minute, as a measure of the productivity. The values were plotted for different contrasts against the brightness values as abscissæ, the latter on a logarithmic scale as shown in Fig. 3. It should be noted that the brightness values of the curves are always the higher values of the contrast relation;

FIG. 3.

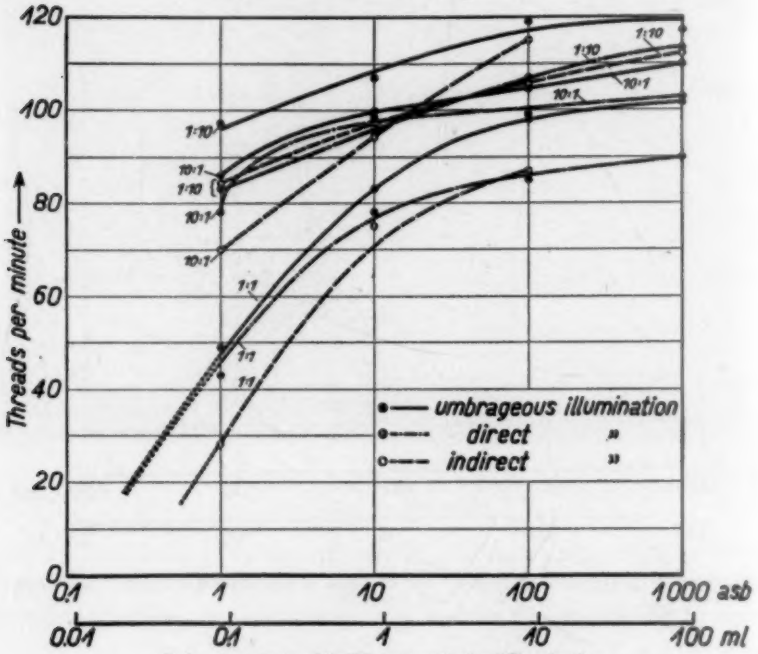


Laboratory tests of productivity with "normal" kind of illumination of different brightness and contrasts.

that means, for instance, for the proportion of 1:10 they correspond to the brightness of the background and for the contrast of 10:1 they refer to the brightness of the threads. The curves show that the productivity increases with the brightness and the contrasts, although the increase is more rapid for the lower brightnesses and slows down in its increase for brightnesses above 1 ml.

In the above set of experiments the illumination was the "normal" of just 2 direct lighting units over the working plane. In a second set of experiments the influence of the "umbrageousness" was determined by taking similar tests as the above for three different methods of illumination. Aside from the normal illumination just described the indirect method and the shadow casting illuminations were used and in each case the 3 contrasts 1:1, 1:10 and 10:1 were kept constant. A higher contrast was not considered necessary as not within the realm of practical application. The results show as in Fig. 4 that at a contrast of 1:10 the conditions are by far the best, and improve also with increased illumination.

FIG. 4.



Laboratory tests with different methods of illumination.

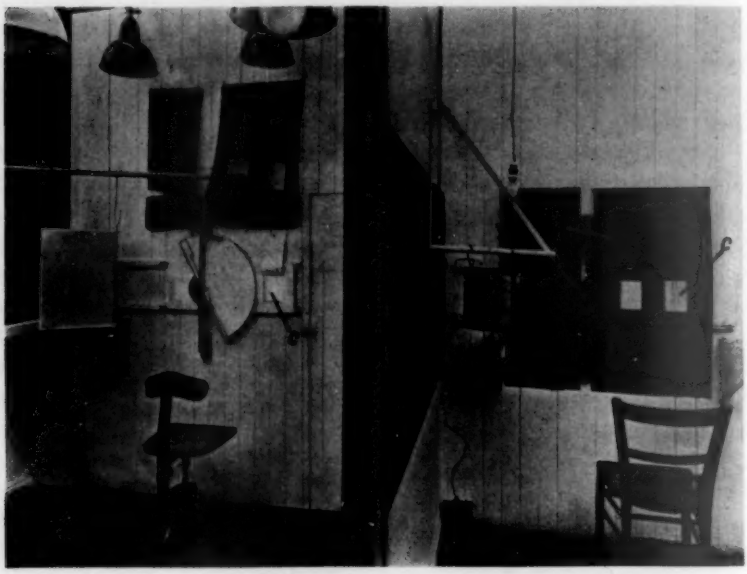
A further series of experiments was then made to determine the influence of the thickness of the threads as well as that of the distance between them or in other words the influence of the coarseness of the woven material. It developed, as was to be expected, that for heavier threads and greater interspaces the productivity was increased, but not in a straight proportion thereto. In the beginning with the thinner dimensions, the improvement was more rapid and became almost constant for the coarsest material. As far as the samples of the working models are concerned, they were, of course, similar to the first one, but had to be larger in order to accommodate 300 threads for the various thicknesses.

The last series of laboratory experiments concerned the perceptibility of defects under various degrees of illumination and contrasts. For this purpose it was necessary to have a special set of devices in order to determine and automatically to control the time of exposure of the working model to the eye of the observers, and in order also to calibrate the automatic devices against a sensitive chronoscope. It was found by experiments with a specially constructed tachistoscope that the exposure of half a second was as satisfactory value for the experiments and the shutter built for this purpose was adjusted so as to expose the working model and close it again about within that period. The exact times were checked on the chronoscope and it was found that the average time of exposure of the centre point of the working model amounted to 0.4726 second and the total time of exposure of any part of the model until its complete shutting lasted 0.580 second. Furthermore it was necessary, in order to give the eye of the observer a chance for adaptation, to provide a second model of equal brightness as used in the test, since the working model was only in front of the eye when exposed. This duplicate model can be seen in Fig. 5 by referring to the square *C* at the right side of the semicircular shutter.

In carrying out the experiments the observer had to look at the auxiliary model for about 5 minutes until his eye was adapted, then he was to cover the adaptation model quickly and the actual test took place by the operation of the shutter. After viewing the actual model the observer had to record the findings of the defects by making a sketch from memory as to

their number and position. The performance was repeated until practically all defects were recorded. The result of the test was then represented by the average number of exposures, taken by the various observers multiplied by a factor expressing the difficulty of sizing up the defects. This factor was

FIG. 5.



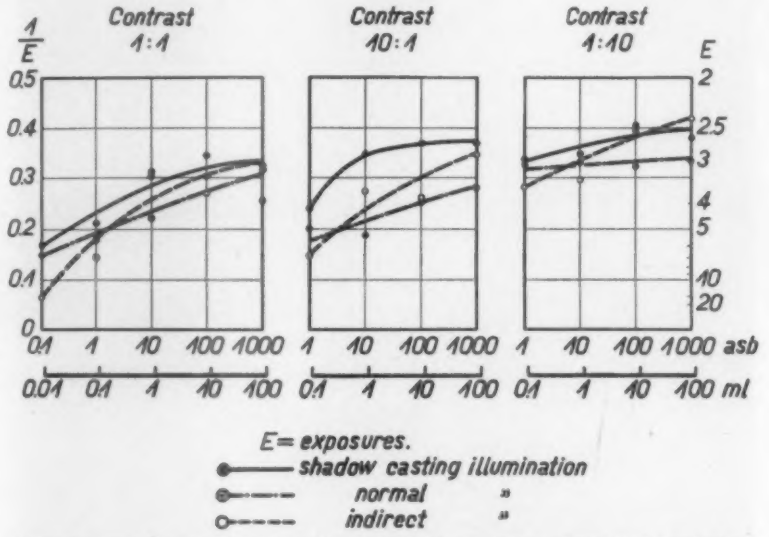
Special devices for laboratory tests on the perceptibility of defects.

arrived at for each working model in advance by a preliminary test with the same observers at normal illumination and a contrast of 10:10 ml. The total values were plotted against brightness for constant contrasts and are shown in Fig. 6. The results are similar as before and show again that the conditions under a contrast of 1:10 and with umbrageous illumination are the best, except that there is an indication that under indirect illumination of very high values of illumination a still better productivity might be obtained.

This finished the laboratory experiments and in order to determine the practical value of the results thus secured and in

order to test them out under actual working conditions, the further investigation was transferred to a wollen mill: Here 4 looms were selected, two of which manufactured light coloured goods of 65 per cent. and 51 per cent. reflection factor and the other two were for dark material of 2.0 resp. 2.8 per cent. factor of reflection. These machines were of a type which

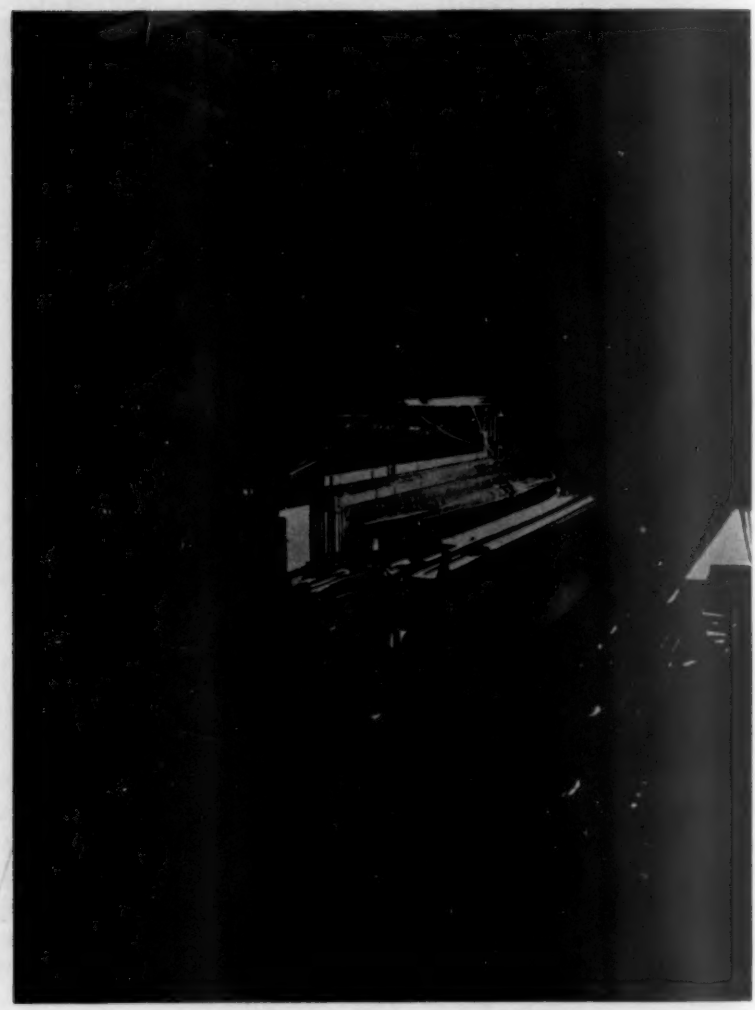
FIG. 6.



Laboratory tests for speed of vision to recognise defects at different methods of illumination.

provided for an automatic stop in case of breaks of woof or warp thread and in case of an empty shuttle, but they were not equipped with automatic devices for change of shuttle. The conditions of illumination as they were found in this mill, are tabulated in Table 1, which includes also the values of the 3 steps of improved illumination that were employed in the tests later on. The type of the improved illumination selected was the umbrageous one, as it had been found the most satisfactory. It was furnished by 2 asymmetrical mirror reflectors (symmetrical reflectors in inclined position) as shown in Fig. 8. This picture gives an idea of the general appearance under the improved illumination, while Fig. 7 is illustrating the old conditions of normal illumination. The angle of incidence of

FIG. 7.



Loom of woolen mill under old "normal" illumination.

the reflectors was chosen as of 35° with the horizontal to suit the practical working conditions and proportions existing in this factory.

In making the experiments every precaution was taken to develop a true and unbiassed picture of the very benefits derived from the improved illumination: For this reason the

TABLE I.

Illumination Values.

	Type of Illumination.	Horizontal Illum. in Footcandles.				Vertical Illum. Footcandles.in	
		Location.	Front.		Rear Working Place.	Front.	Rear.
			Working Place.	Shuttle.			
1.	Original or "normal"...	Em	12.8	7.9	12.6	5.45	3.8
		g	21.2	37.8	24.4	16.8	22.8
2.	Improved Step 1.....	Em	23.7	18.8	17.8	8.45	9.6
		g	49.3	70.5	35.6	35.5	40.2
3.	Improved Step 2.....	Em	39	30.0	21.6	20.4	8.82
		g	42	11	28.6	51.8	31.4
4.	Improved Step 3.....	Em	168	133.0	132.0	95.0	19
		g	70	23.9	28.6	77	20.5

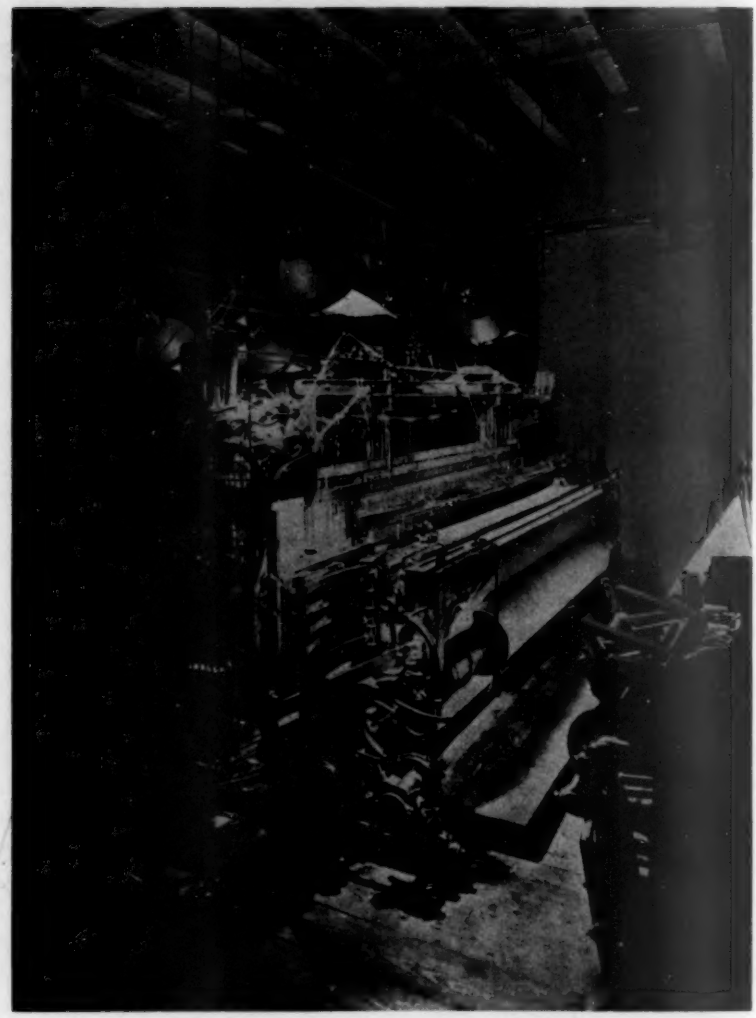
Em = average illumination.
g in per cent. degree of uniformity.

same weavers were kept at their loom and the material employed at each loom (woof and warp thread) was not altered throughout the whole series of the test runs.

Psychological factors that might affect the men under the new conditions were watched carefully, such as the disturbance caused by the tests, the suspicion aroused, the disinclination of improving the output etc. It may be said, however, that the class of working men was of such a type that they did not influence the reliability of the tests.

On the other hand the stimulation caused by the improved illumination might have possibly distorted the results. By way of explanation of the psychological considerations involved herein it may suffice to say that the stimulation given a working man by improved working conditions, such as better

FIG. 8.



Loom of woolen mill under improved illumination.

illumination, manifests itself in two ways: at first in an impulse limited in time which wears off gradually and secondly in a lasting effect of greater ease. To balance these two stimuli half of the tests were run with rising and the other half with decreasing illumination.

It furthermore was necessary to eliminate from the records all activities that might introduce an error or even a doubt into the results. Thus the gross working times were taken at intervals with the aid of a stop-watch, and all times and stops and their reasons were carefully recorded, analysed and the operating period reduced to a net value by deducting all these actions and stops of the work, which were not inherent nor to be attributed to the performance of the regular work, such as repairs of the machine, short absence of the workman or the like.

A correction was also applied to take care of the elements of chance, such as non-uniformity of the thread causing more or less numerous breaks at different times, the weather, the physical conditions of the men, etc. By taking the conditions as they existed during the test under the old illumination as a guide, the values were reconciled to a uniform performance of a "constant run" under like conditions.

With all these considerations in view a true picture of the essential facts could be derived from the tests.

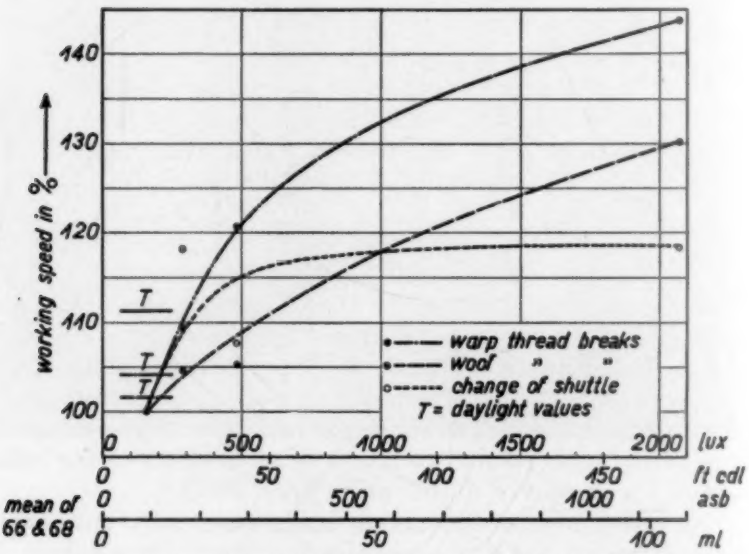
Now, it is obvious that the ultimate criterion of the economy effected by the improved illumination is expressed by the quality and quantity of the material that is turned out within a given period of time under the different degrees of illumination.

Leaving at first the question of quality out of consideration, a measure of the quantitative output can, of course, be regularly obtained by means of the "shoot-counter" attached to the shaft of most of the looms. Here, however, the readings of the counter served only as a check on the totals of the test-results, while the investigations had to be carried on as they were, to provide for an insight into the individual operations of the weavers and to admit of an analysis of the influence of the improved illumination upon them.

Now the process of weaving being essentially automatic, requires visual activity necessitating good illumination in

order to take care of such work as to watch for imperfections of the thread, repair breaks of the warp as well as of the woof threads, change of shuttle, etc. All these operations involve stoppages of the loom. Thus it is obvious that the quantitative gain that may be derived from improved illumination and which ultimately will manifest itself in increased production, must necessarily accrue from a reduction of the "number" and "duration" of the stops. The latter indicates increased working speed, the former is the result of enhanced perceptibility. Both factors, duration and number of stops, have been analysed separately by taking the "net" values of the various individual operations which, as described above, had been shorn of all irregularities. The increased working speed was derived for the three predominant operations (breaks of warp and woof threads and change of shuttle) by comparing the net working time for each operation with the time taken under "normal" operation (old illumination). The reciprocal of this percentage value furnishes then the increased working speed and is plotted in Figs. 9 and 10 as a function of the increasing illumination.

FIG. 9.

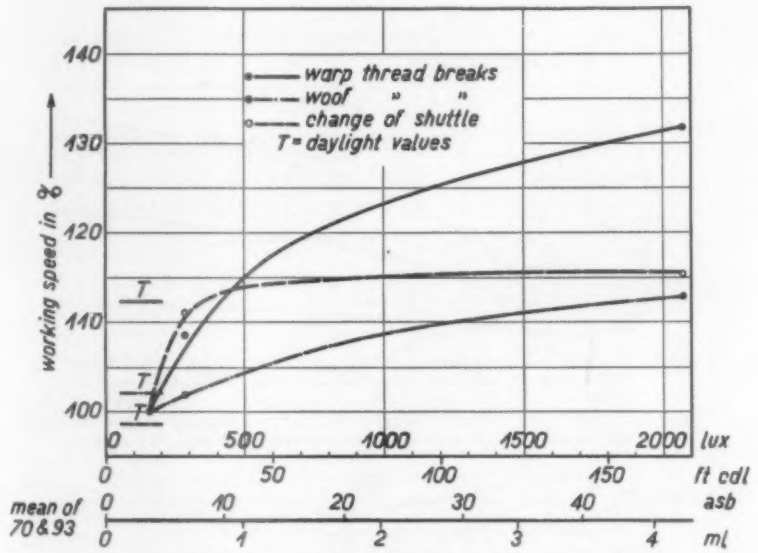


Factory tests for reduction of duration of stops for light material.

From these curves it becomes apparent that the saving in time for the operation of repairing breaks of the warp threads shows much higher values than for the other operations, and is therefore by far the most important for the total increase in working speed.

The influence upon the number of stops may be analysed in such a manner: As the looms used have no automatic devices to effect a change of shuttle, it is evident that there

FIG. 10.



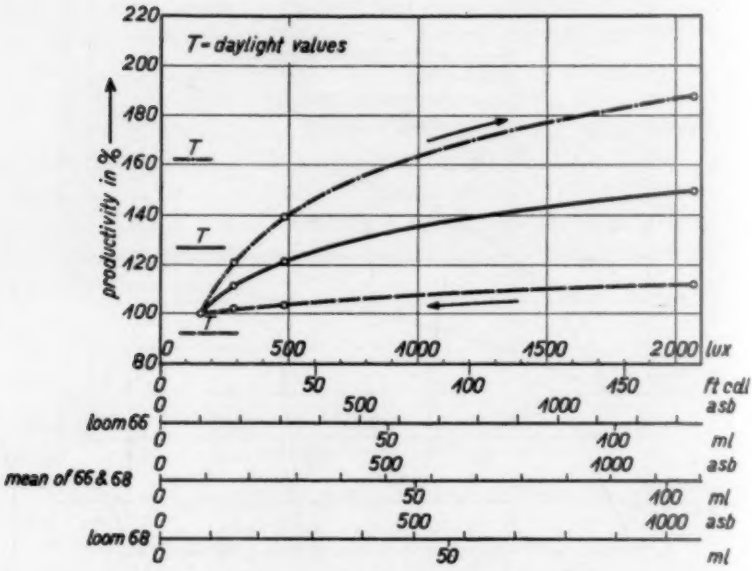
Factory tests. Reduction of duration of stops. Dark material.

must be a number of stops which is a regular minimum depending on the number of changes of shuttle, necessary for a certain kind of material, and that beyond this minimum, no reduction of the number of stops can take place. But, as a result of quick recognition and consequent action facilitated by improved illumination, the automatic stops may be anticipated and considerable time thus saved in as much as then the threads do not become seriously entangled or the end of the warp thread could be more readily located. It is therefore the reduction of the number of automatic stops which

signify a saving of time or an increase of productivity. Further than that, through good illumination, the operator may also be in a position to watch and "nurse" the thread and thus avoid breaks of the threads and consequent stops prophylactically.

From the results of these observations covering "number" and "duration" of stops, the total increase of productivity has been determined, and is shown in Figs. 11 and 12. It will

FIG. 11.

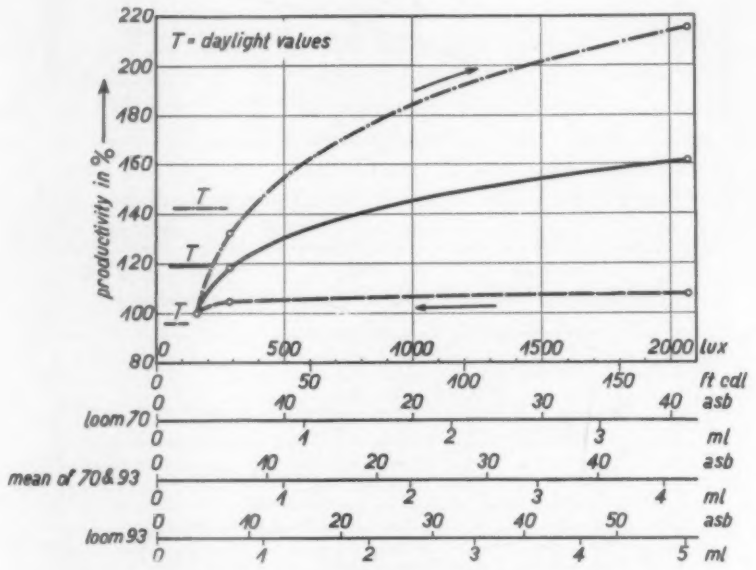


Results of factory tests. Total productivity for light material.
—.—.— Loom 68.
— — — — Loom 66.
———— mean of both.

be noted that there is a great difference of performance between the work of the weavers at looms 66 and 68 and likewise 70 and 93. This discrepancy is explained by the fact that in order to eliminate the influence of "stimulation" referred to above, the illumination was changed in steps of increasing illumination for one set (66 and 93) and of reducing illumination for the other set (68 and 70). The mean of the two rep-

resents the conditions fairly accurately, and thus in Fig. 13 the total increase of productivity is shown in percentage relation to the "normal" illumination. At the same time the "loom" efficiency is indicated on the right hand scale of the diagram. As to this efficiency it may be stated that it was

FIG. 12.

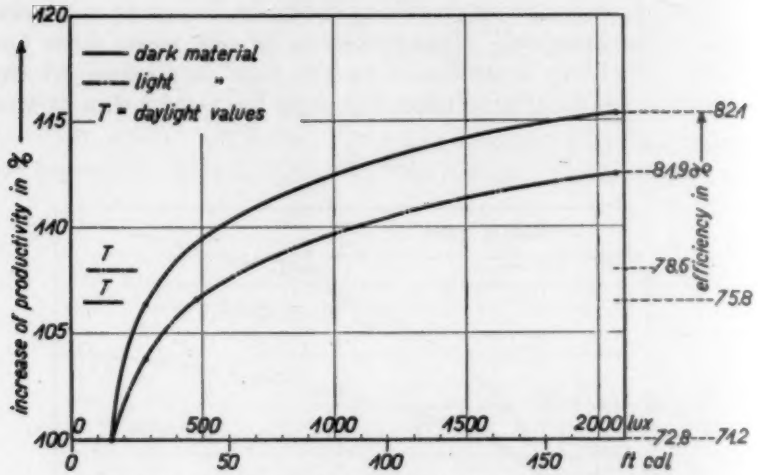


Results of factory tests. Total productivity for dark material.
—.—.— Loom 70.
– – – – Loom 93.
——— mean of both.

figured to be 100 per cent. if the loom were operated uninterruptedly that is without stops of any kind, an assumption which could not be realized with these looms as there was no automatic change of shuttle.

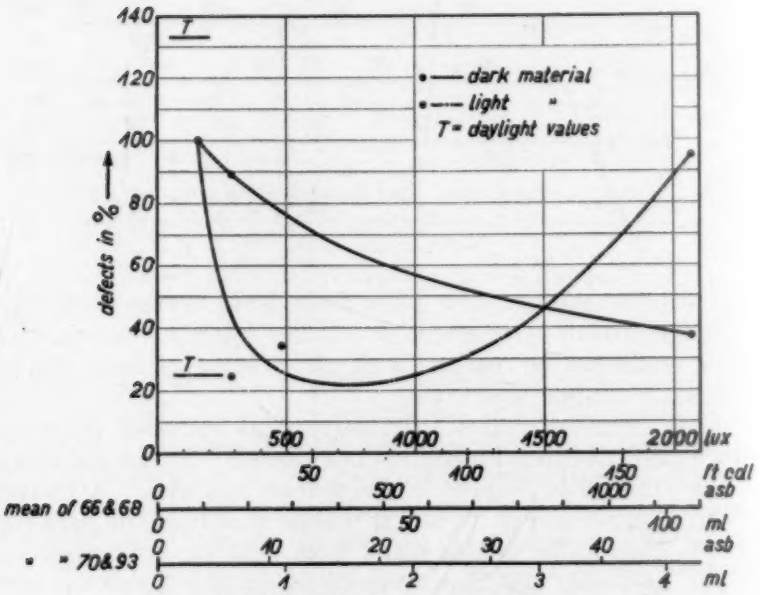
Besides these quantitative gains thus recorded there are also qualitative accomplishments expressed by the reduction of the number of defects in the woven material. A picture of this is given in Fig. 14 and it will be seen that the performance is quite different for black from that for light material. In the first case the improvement in quality keeps up with increasing illumination and could probably be increased

FIG. 13.



Factory tests. Increase of efficiency through improved illumination.

FIG. 14.

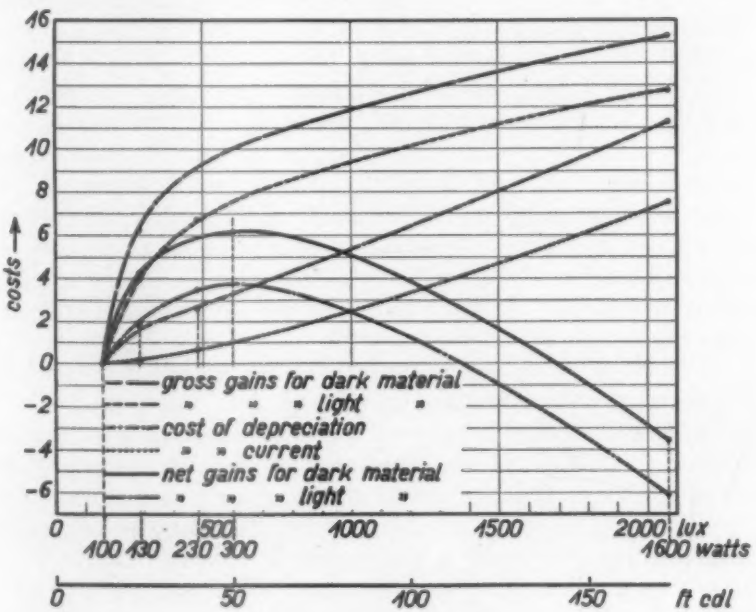


Factory tests. Reduction of defects. Qualitative gains.

further, while for the light material the defects reach a minimum at an illumination of about 75 ft. cdl. and start to increase again in numbers, if the illumination exceeds 100 ft. cdl.

In order to derive the economy effected by the improved illumination, one has to determine not only the increase of efficiency, but has also to consider the higher expense involved thereby. The latter is due to higher current consumption as well as to an amortization of the additional capital invested for the alterations. Of course, the rates for electric current and the cost for material and labor are different in Germany from those in the U. S. A. and therefore the economical aspect will be different and will have to be determined specially. But in view of the fact that labor is higher in U. S. A., its influence will be the determining factor and the figures in U. S. A. would show an undoubtedly still better appearance. As pictured in Fig. 15 the German figures reveal that at an

FIG. 15.



Economy of production.

illumination of 60 to 70 ft. cdl. the economy curve has a maximum and decreases from there on, which means that in this type of textile mills and under the conditions as explained, the illumination should be raised to the above value, in order to reach an economical optimum.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

QUARTZ PLATE MOUNTINGS AND TEMPERATURE CONTROL FOR PIEZO OSCILLATORS.

During the past few years an extensive study of certain phases of piezo oscillator construction and performance has been made at the bureau. The oscillators studied have been those sent in for calibration and those built at the bureau to serve as frequency standards. In a report published in the October number of the Bureau of Standards Journal of Research the quartz plate mountings and the temperature-control units will be discussed.

The quartz plates commonly used are either rectangular or circular. For frequency standards the electrodes of the plate mounting should be so spaced (1) that the air-gap does not change with time; (2) that the air-gap changes in a definite manner with variation in temperature; and (3) that all unessential electrical capacity is minimized. The shifting of the quartz plate between the electrodes must be as small as possible.

A simple type of holder, which is often used for rectangular quartz plates, consists of two brass electrodes with a celluloid or bakelite ring to partially limit the shifting of the quartz plate. The upper electrode may be adjustable as to air-gap or may rest on the quartz plate. Since the quartz plate changes its position with any slight jar the frequency is ordinarily constant only to 1 part in 10,000 to 30,000.

A quartz bar may be held in position in the mounting by two screws mounted in the lower electrode in such a way that they engage in slots in its edges, one in each edge midway between the two ends. Bars mounted in such a manner are found to be constant in frequency to 1 part in 300,000.

Another method of mounting a long rectangular quartz plate to oscillate in its extensional mode is to clamp it centrally with respect to its ends between two narrow surfaces project-

* Communicated by the Director.

ing from the electrode faces in such a manner that the narrow contracting areas are perpendicular to its length. Quartz spacers fix the air-gap. This type of holder is very satisfactory for any plate whose extensional vibration frequency is below 100 kc. The constancy of frequency is about 1 part in 300,000.

A circular quartz plate is somewhat easier to mount satisfactorily than a rectangular one. A simple type of mounting for circular plates uses a piece of pyrex tubing, slightly larger in diameter than the quartz plate, to serve as a spacer between the electrodes as well as to hold the quartz plate in place. The greatest possible constancy in frequency for a plate in such a mounting used in a portable standard is 1 part in 200,000.

For the "thickness frequency" a hole, tapering in from each face, may be cut along the cylindrical axis of the quartz plate. This decreases the temperature coefficient of frequency. The plate is them mounted on a horizontal bakelite rod passed through the hole. A pyrex ring serves to space the electrodes. Although a quartz plate mounted in this manner is not reliable in a portable standard, in a fixed position the frequency will be reliable to 1 part in 1,000,000.

It is possible to mount a circular quartz plate so that it will be reliable as a portable standard. About the cylindrical surface a V-shaped groove is cut half-way between the plane faces of the quartz plate. The plate is then mounted within a metal ring by 3 screws, 120° apart, whose tapered points fit in the groove to grip the plate. The metal of which the ring and screws are made should be chosen so that the expansion of the quartz plate is the same as the differential expansion of the ring and screws. Pyrex washers space the electrodes on each side of the quartz plate. In such a mounting the decrement is small and there is no chance of the quartz plate shifting in its mounting. The frequency of a portable standard using such a mounting will remain constant to 1 part in 1,000,000 with the oscillator circuit temperature-controlled.

The simplest type of temperature control consists of a small box of wood or similar material, containing the quartz plate, a thermostat, and electric heater. The relative locations of these various elements in the cabinet, and the type

of thermostat determine the constancy of temperature control. A good bimetal thermostat will hold the temperature constant to 1° C.; a mercury thermostat will be probably ten times as constant.

The quartz plate may be placed inside a heat-attenuating box within the temperature-controlled compartment. This attenuating box may be of wood, or better, of alternate layers of metal and felt or asbestos. Such attenuation ordinarily decreases the variations of temperature at the quartz plate to 1 per cent. of that of the temperature-controlled space.

Where greater constancy of frequency is desired, the oscillator circuit must be maintained at constant temperature. It is more desirable to have a double temperature-control on the quartz plate, putting the oscillator circuit in the outer control compartment together with the attenuating box containing the inner temperature-controlled space and the mounted quartz plate.

A BALANCED THERMOCOUPLE AND FILTER METHOD OF ULTRA-VIOLET RADIOMETRY.

At present the physician has neither a unit of dosage nor a meter for accurately measuring the amount of ultra-violet radiation used for healing purposes.

In the absence of an inanimate dosage-meter the patient is used as an indicator, and the dosage is estimated by the erythema produced on some untanned part of the body, e.g., the inner forearm, when exposed to the lamp. It is probable that this precautionary test of exposure to ultra-violet will always be made. However, in view of the wide variation in erythemic susceptibility of pigmented and unpigmented skin, burns are likely to be produced and the search in progress, the world over, is for a simple device for accurately measuring the ultra-violet intensity of the source used for healing purposes. In this search, the Bureau of Standards and other research laboratories are taking an active part; particularly the bureau, in the problem of standardization of ultra-violet intensity or so-called dosage meters.

A paper which was published in the October number of the Bureau of Standards Journal of Research (Research Paper No. 370), is a further contribution (see B. S. Research Paper

No. 318) to the investigation of filter radiometry, with special reference to the quantitative measurement of the component of ultra-violet radiation, of wave-lengths less than 313 millimicrons in sunlight and in artificial sources, which biologists recognize as of special importance in the prevention and cure of rickets.

The apparatus used was a balanced radiometer, consisting of a thermocouple in which the two receivers are simultaneously exposed to radiation, under which conditions practically no thermoelectric current flows through the galvanometer. A 1-cm. cell of water or of crystal quartz was used continuously over the thermocouple receivers.

On covering one receiver with a filter that excludes the ultra-violet which it is desired to evaluate and the other receiver with a window that freely transmits these ultra-violet rays, and exactly balances the transmission losses of the exclusion filter, throughout the remaining part of the spectrum, the galvanometer deflection obtained on exposure of the two thermocouple receivers through this combination of filters is a direct measurement of the ultra-violet emitted by the source under investigation. In order to evaluate the ultra-violet of wave-lengths less than 313 millimicrons, it is necessary to know the relative spectral energy distribution of the source for wave-lengths less than 400 millimicrons.

The ultra-violet exclusion filter was a barium flint glass and the balancing filter was of crystal quartz or Corex G980A, depending upon the source of radiation. The lack of complete balance of long wave-length radiation was determined by covering both receivers with a plate of Noviol-A glass, which is opaque to radiation of wave-lengths less than 400 millimicrons, the long wave-length end-point of absorption of the barium flint exclusion filter.

Using two arrangements of (1) the balanced pair of thermocouple receivers with a single exclusion filter method, and (2) a single thermocouple receiver with two exclusion filters (three methods in all); and (3) using two methods of calibrating the radiation sensitivity of the thermocouple receivers in absolute units, closely agreeing measurements were made showing that the average amount of ultra-violet radiation of wave-lengths less than and including 313 millimicrons for

midlatitude sea level stations, during the clearest weather, during midday in midsummer, amounts to about 90 microwatts per cm^2, decreasing to about 20 microwatts per cm^2 on the clearest days in midwinter.

An experimental procedure is described for testing the performance and for standardizing photoelectric cells, for use as ultra-violet intensity (so-called dosage) meters.

An experimental procedure is described for using measured amounts of spectrally pure ("monochromatic") and of heterogeneous ("heterochromatic") ultra-violet radiation in physiological tests, such as, for example, the amount of ultra-violet energy required to produce a minimum perceptible erythema on the untanned human skin. Data are given showing the erythemogenic efficiency of Washington midsummer ultra-violet solar radiation is only about 21 per cent. that of the wave-length (297 millimicrons) of maximum erythemic susceptibility. Using the spectral erythemic response curve observed by the writers, the calculated erythemogenic efficiency is 22 per cent. which is as close an agreement as can be expected, in view of the uncertainty in the ultra-violet solar spectral energy curve upon which the calculations must be based.

Using an artificial source of radiation in which the ultra-violet spectral energy distribution and the total erythemogenic ultra-violet radiation could be accurately measured, the observed time of exposure to the total radiation from the lamp, required to produce a minimum perceptible erythema, was in good agreement with the time calculated from observations using the wave-length (297 millimicrons) of maximum erythemic susceptibility.

SOLARIZATION AND REJUVENATION OF WINDOW GLASS.

In previous reports (Technical News Bulletins Nos. 152, December, 1929; 160, August, 1930; 164, December, 1930) attention was called to the fact that short wave-length ultra-violet radiation of wave-lengths less than about 320 millimicrons in sunlight and in artificial sources have the property of decreasing the ultra-violet transmission of certain special glasses to a stabilized value. Further exposure of these

glasses to radiation of wave-lengths longer than about 350 millimicrons in the mercury arc and in sunlight (which are isolated by covering the glasses by filters of window glass, etc., that are opaque to the short ultra-violet rays) increases the transmission to an appreciably higher value. In one test the rejuvenated transmission under the filtered mercury arc was higher than that of a duplicate sample exposed to filtered sunlight. This is probably owing to the fact that after filtering the wave-lengths shorter than 313 millimicrons from the radiation from the mercury arc but little remains other than the 365 millimicron line.

During the past summer these tests were repeated and verified, by exposure of the special glasses under (1) black paper, (2) quartz, (3) window glass opaque to wave-lengths less than 313 millimicrons, and (4) a filter of G584 glass that is opaque to wave-lengths less than 340 millimicrons. The heating under the black paper produced no change in transmission. The decrease in transmission under quartz was practically the same as unfiltered sunlight. The increase in transmission under window glass was less than under the blue green filter G584 which verified previous tests showing that wave-lengths in the region of 365 millimicrons have the greatest rejuvenating action.

Present experience indicates that the use of filtered radiation from the quartz mercury arc is less reliable than unfiltered radiation in making stabilization transmission tests. Inconsistencies reported by others may be owing to the fact that the natural solarization tests of the window glasses were made in the autumn and in January to March, when owing to the low altitude of the sun, the shortest ultra-violet rays are absent and the stabilized transmission is not so low as is obtained in summer sunlight.

Stabilization tests requiring 200 or more hours exposure to be filtered radiation are impracticable. Hence, as described in Technical News Bulletin No. 162 of October, 1930, the most reliable procedure is to stabilize the transmission by exposure to the unfiltered radiation from the quartz mercury arc lamp.

FUNDAMENTAL STANDARDIZATION OF COLORS.

Because of their impermanence, material standards, such as glass filters or colored chips, can play only an auxiliary part in the standardization of color on a fundamental basis. The fundamental specification consists of a spectral distribution of energy, which is the immediate stimulus for the color, combined with the color-vision characteristics of the eye whose activity results in the color. The spectral distribution of energy taken alone is sufficient to insure the reproduction of the color, but, taken along, it would be an unduly stringent specification because it would exclude many other distributions of energy which result in the same color. It is customary, therefore, to express color specifications in terms of a normal eye to which, for the sake of uniformity, all distributions of energy serving as color stimuli are referred. The "excitation" curves of the Optical Society of America, based on measurements taken by Abney and König more than 20 years ago, have been widely used in America to define the properties of a normal eye for the purposes of color standardization.

Recently a British investigator, Doctor Wright, has repeated for ten observers the measurements of Abney and König using improved apparatus and technique, but, because of the form in which the results were expressed, it has not been possible to compare his results with the O. S. A. "excitation" curves directly. The requisite transformations have now been carried out in the colorimetry section of the Bureau of Standards, and it is disclosed that Wright's results check those of Abney and König except for differences which are not large compared to individual variations. It is concluded, therefore, that the slightly more faithful representation of normal vision afforded by Wright's data is not sufficient to justify the inconvenience of supplanting the present standard. However, the O. S. A. "excitation" curves have other defects which hinder their technical application more than their failure to give faithfully the characteristics of normal vision.

It is possible that to remedy all these defects would make a change in these standard data worth while, even though subsequent projects in color standardization would have to be carried out on a basis not comparable to those already accomplished.

POROSITY OF ELECTROPLATED CHROMIUM COATINGS.

Although chromium plating is very extensively applied to automobiles and other finished metal articles, it is well known that the chromium deposits are usually porous, and that the protection against corrosion of the base metal depends principally upon the quality of the nickel and copper coatings that almost invariably precede the chromium, In a research, made by the Bureau of Standards in coöperation with the American Electroplaters' Society, methods for detecting and evaluating the porosity of the chromium deposits were investigated, and the factors that influence porosity were studied.

Various methods that have been described for detecting porosity in chromium deposits were found to yield consistent results. The most generally applicable and reliable is the copper deposition method, which depends on the fact that under certain conditions copper will not deposit on chromium, but only in pores or cracks in the chromium. This method was made semiquantitative by measuring either the average apparent current density or the weight of copper deposited in two minutes at 0.2 volt. The results represent the relative porosities. In order to determine whether a decrease in porosity of the chromium will result in an increased protective value, exposure tests are being made in coöperation with the American Electroplaters' Society and the American Society for Testing Materials. The following conclusions are therefore tentative.

Very thin deposits of chromium usually contain round pores. As the thickness is increased, these pores disappear but cracks are formed, especially on standing. For the common conditions of deposition, the minimum porosity is obtained with a thickness of about 0.00002 inch, which is the usual thickness applied to automobile parts. If, however, the chromium is deposited at a higher temperature such as 65° C. (149° F.) instead of the usual temperature of 45° C. (113° F.), and at a suitable current density, the deposits are less porous than usual. This is especially true of thicker deposits.

The least porous deposits are produced on nickel, which is generally applied as a preliminary coating on other metals

before chromium plating. Heating the deposits to 200° C. for a short time produces a greater porosity than if they were allowed to stand at ordinary temperature. Under the latter conditions the porosity gradually increases for two weeks.

If the results of these laboratory studies are confirmed by exposure tests, it may be possible to improve the protective value of the chromium coatings by using higher temperatures and sufficiently high current densities to produce bright deposits.

A complete report on this study was published in the October number of the Bureau of Standards *Journal of Research.*

THERMOMAGNETIC PHENOMENA.

Steel upon heating or cooling undergoes characteristic magnetic transformations which are associated with corresponding structural transformations. The observation of these magnetic transformations with special reference to their interpretation in terms of the corresponding changes in structure or condition has been termed thermomagnetic analysis.

In a paper before the September meeting of the American Society for Steel Treating in Boston, R. L. Sanford of the bureau discussed the characteristic magnetic phenomena which may be observed when steel is heated or cooled, and showed how they may be interpreted in terms of the corresponding structural transformations. Thermomagnetic analysis, on account of its great sensitivity, offers a means for studying some changes in the structure of steel which can be observed in no other way.

THERMAL EXPANSION OF FERROUS ALLOYS.

With the coöperation of a number of steel companies and other manufacturers of heat resisting alloys there was recently completed at the bureau a comprehensive investigation on the linear thermal expansion of various commercial nickel-chromium, iron-chromium, and nickel-chromium-iron alloys. These alloys contain 0 to 77 per cent. nickel, 5 to 27 per cent. chromium, and 0 to 82 per cent. iron. The coefficients of expansion of the alloys were determined for various tempera-

ture ranges between 20° and 1000° C., and the effects due to temperature, chemical composition, heat treatment, etc., were determined. Critical regions were located on the thermal expansion curves of some of the alloys. The data which will be published later in the Bureau of Standards *Journal of Research*, are useful in several ways: It is possible to select heat resisting alloys which have the same coefficients of expansion for a given temperature range as other materials, for example, brass, copper, procelain, steel, etc., when assembled in equipment or appliances where differences in expansion would be undesirable. It is possible to predict the coefficients of expansion of similar new alloys. It is also possible to determine the heat treatment suitable for each type of alloy for a specific purpose as governed by the desired structure.

During the past year the coefficients of linear expansion of a number of samples of invar and related nickel steels were determined. These alloys were used in level rods, side bars for strain gages, elevator hoistway interlocks, etc., where low expansion is necessary.

About 50 tests have been made during the year.

AQUEOUS SOLUTIONS FOR QUENCHING STEEL.

Steel is an alloy with ability to develop properties covering a wide range of strength, hardness, and ductility. It is because of this versatility and adaptability that steel plays so important a part in modern life and industry. One of the most important duties of the metallurgist is to determine the treatments to which any given steel must be subjected to develop the properties needed in some particular service. The more common steels are made soft by cooling slowly from temperatures approximating a "red heat," and are hardened by cooling rapidly from these same temperatures.

Quenching, that is, cooling rapidly from a red heat by plunging metal into water or oil, is thus a fundamental process in heat treatments employed to develop enhanced properties in steel. The precise structure and hence properties produced in quenching are controlled by the speed at which the steel cools during the operation. Water and oil are the

two most commonly used quenching media. Water produces the more rapid cooling effect, that is, a steel quenched in water is in general harder than if quenched in oil. Occasionally a water-quenched steel is too hard for the most satisfactory service. In such a case a tempering treatment is frequently necessary, which consists of reheating the steel after quenching to relative low temperatures.

A steel equivalent to or possibly better than the quenched and tempered steel would often be possible if quenching solutions were available possessing characteristic cooling rates between those of water and oil.

In a recent investigation at the bureau a study was made of aqueous solutions of ethylene glycol, glycerine, and sodium silicate to determine whether any of them offered promise as quenching media with characteristic cooling rates in this intermediate range. It was found that the solutions of glycol and of glycerine did not give results which were readily reproducible. Hence, such solutions do not appear promising for practical use. However, solutions of several concentrations of sodium silicate proved to have quenching rates in the desired intermediate range and to give very consistent results. Some of these sodium silicate solutions must be treated with small additions of caustic soda in order to prevent changes in them when allowed to stand for several months. The effect of varying the concentration and the temperature of the sodium silicate solution was studied. It was concluded that sodium silicate solutions give promise of usefulness in the quenching of steels by providing solutions having graded cooling rates between those of water and of oil.

A full report on this subject was published in the September number of the Bureau of Standards *Journal of Research*.

FIRE TESTS OF PARTITIONS.

The evolution of modern types of fire resistive building construction has brought about improvements in the use of the older building materials and the development of several new ones. Among these is a structural unit, introduced in Europe, the manufacture of which has recently been started in this country. This unit is made by thoroughly coating

long woodshavings (excelsior) with a magnesium cement and moulding the coated mass of fibers into the desired form. The cement coating serves the double purpose of flameproofing the wood and binding the fibers into a unit of the necessary degree of rigidity. Both insulating and building units are made.

Fire endurance, fire, and fire hose stream tests on plastered partitions of these blocks, 16 feet long by 11 feet high, were conducted recently in the bureau's wall testing furnace. These partitions were built of blocks 3 inches thick and plastered on each side with approximately 1/2 inch of sanded gypsum plaster. The first of the test partitions was built of blocks manufactured in Europe. These blocks were 1.6 meters (63 in.) long by 0.5 meter (20 in.) high by 7.5 cm. (3 in.) thick. This partition was reinforced with three No. 10 gage wires placed vertically on each side, at the center and quarter points of length, and anchored to the restraining frame of the furnace at top and bottom. Tie wires through the horizontal joints between courses bound the wires on the opposite sides of the partition together. These reinforcing wires were placed during the construction of the partition and covered in by the plaster. The other partitions were built of blocks of domestic make 48 inches long, 20 inches high, and 3 inches thick, set in the same manner except that there was no wire reinforcement.

The partition built of European blocks and one built of domestic blocks were tested for fire endurance. The end point for each test was determined by rise of temperature at one of the nine thermocouples by which the surface temperatures were measured, this temperature being more than 30 per cent. in excess of the general average of all the surface temperature measurements. The rise in each case was 181° C. (325° F.) above the initial temperature and was reached at 2 hours 12 1/2 minutes and 2 hours 18 1/2 minutes, respectively, in the two tests. The average rise of the temperature at the nine points was in each case much below the limit of 139° C. (250° F.) permitted by the standard fire test specification. In the first test this rise was 108° C. (194° F.) and in the second 90° C. (163° F.).

In neither case did the fire break through the partition subsequent to the fire test. In the first test, however, glow

continued in the blocks for about 2 1/2 hours after the furnace fire had been stopped, influenced to a large extent by the high temperature of the confronting furnace wall. The partition was removed from the furnace after 2 hours 24 minutes in the second test and subjected to a hose stream. The excelsior of the blocks in this test was found to have been charred to within 1/2-inch of the plaster on the unexposed side of the partition.

A partition built of blocks of domestic manufacture was subjected to fire for one hour and subsequently to impact and erosion effects of a fire hose stream from a 1 1/8-inch nozzle on a 2 1/2 inch fire hose, the pressure at base of nozzle and duration being approximately equivalent to 4 2/5 minutes application at a water pressure of 30 lbs./in.^{2} The partition withstood this test without passage of flame, hose stream, or unduly high temperature. In this test the wood shavings were charred to depths of 1 3/4 inches from the fire exposed side of the units, but the average depth of char was approximately 1 1/4 inches. In a few small areas the stream eroded the block materials to within 1/2 inch of the plaster on the unexposed side.

As based on performance in these tests, this partition construction develops a fire resistance of 2 1/4 hours, combustible, as tested according to established procedure.

MASONRY CEMENTS.

A study of masonry cements and mortars has been undertaken at the bureau. Certain hitherto unmeasured properties, such as plasticity, water-retaining capacity, and volume change are being studied, and further workability, an essential property in masonry cementing materials, is being given particular attention. The compressive strength of 2-inch mortar cubes is also being determined.

Plasticity is measured in accordance with the principle employed in the McMichael viscosimeter, i.e., shearing of the material by a fixed body in a rotated cup. The water-retaining capacity is measured by exposing one side of a thin slab of the mortar to a slight vacuum for various periods of time. This simulates the water withdrawing action or "suction" of a brick.

Volume change is measured from the time the mortar is mixed, through long storage periods when stored both at 60–70 per cent. relative humidity, and inundated. Six specimens of the mortar are cast in a vertical manifold watertight mold containing six 1 by 1 by 8 inch compartments with glass plates cast in each end of the specimen. Immediately after filling, the mold is placed under six dial strain gages—one gage for each specimen, by which the shrinkage is measured through the setting period. When the specimens have hardened sufficiently they are removed from the mold and placed in damp closet storage for one week after which they are subjected to the two storage conditions already described. Comparator measurements are made daily for the first week after removing from the molds, weekly for one month, and monthly from that time on. The cubes are made in three consistencies. They are stored one week curing in the damp closet, one week inundated, and finally one-half are placed in air at 60–70 per cent. relative humidity, the other half being kept under water. Cubes are broken at 7 and 28 days, 3 months, and 1 year after the date of making.

The study of the interesting property of volume-yield has been added to the investigation. This includes density determinations of the masonry cements both dry and in the neat mix. Certain devices for the measurement of the above mentioned properties have been developed during the investigation and they are now being used on some 40 or more masonry cements now on the market.

PERFORMANCE OF AUGER MACHINE FOR EXTRUDING CLAY COLUMNS.

The factors involved in the design of dies and augers for extrusion machines used in the manufacture of heavy clay products, are being investigated at the bureau. The experimental apparatus consists of a combined pug mill and auger machine of a very modern type. The various augers are interchangeable, and the dies are so constructed as to make possible any desired change in length, taper, or core design. A series of several extrusions is made with each change in set-up of auger or die. During the course of repeated extrusions, the

moisture content of the clay decreases by evaporation, and moisture determinations are made on the clay used in each run, as well as a determination of the actual pressure required to extrude the clay at a definite rate from a closed cylinder. Thus, with both the moisture content and "workability" of the clay determined, reasonably accurate comparisons of data from each series of extrusions can be made.

The total amount of power delivered to the assembly is measured as well as "power consumed" and "power developed" by the auger itself. This affords a means of comparison of the actual mechanical efficiency of any particular type of auger as well as its effect upon the production efficiency.

With the die and core combinations thus far used, the single wing auger has proven most efficient mechanically, with the double and triple wing augers following in order. However, the triple wing auger has been the most proficient from a production standpoint, extruding about 19 per cent. more clay by weight than the single wing and about 23 per cent. more than the double wing auger. But the power consumption when using the triple wing auger was 85 per cent. in excess of that when using the single wing auger, indicating a considerably higher power cost per unit of production.

Variation in moisture content does not appear to have any marked effect upon the order of these comparisons, although an increase of 8 to 10 per cent. in moisture of the clay will decrease the power required by the triple wing auger by more than that consumed by the single wing auger. However, the product is not quite so good in quality as that obtained with a stiffer clay-water mix. Throughout the change in moisture content the proficiency in production of the machine decreases as the moisture content decreases, while the actual mechanical efficiency of both the assembly and the auger alone increases as the moisture decreases.

Synthetic Methionine. Methionine is gamma-methylthiol-alpha-amoni-normal butyric acid. In the lævo rotatory form, it occurs in the molecule of certain proteins, such as casein. Wallace Windus and C. S. Marvel of the University of Illinois have separated racemic synthetic methionine into its two optically active constituents by conversion into the formyl derivative, and crystallization of the brucine salt of the latter. The two formyl derivatives were then obtained from their respective brucine salts by treatment with barium hydroxide. The formyl group was removed by means of hydrochloric acid; and the amino acid obtained. In this manner, both the lævo and the dextro isomers were obtained. The synthetic lævo isomer was found to be identical with natural methionine.

J. S. H.

Fluorides in Potable Waters. H. V. CHURCHVILLE (*Ind. and Eng. Chem.*, 1931, *23*, 996–998) has tested the municipal water supplies of 26 cities for the presence of fluorides. The water from 10 cities east of the Appalachians was free from fluorides that from 16 cities west of those mountains contained fluorides although the concentration of fluoride ion was always less than 1 part per million. Five additional samples from western regions, in which the dental defect known as mottled enamel is endemic, contained from 2.0 to 13.7 parts of fluoride ion per million parts of water.

J. S. H.

Volumetric Determination of Sodium. J. T. DOBBINS AND R. M. BYRD of the University of North Carolina (*J. Am. Chem. Soc.*, 1931, *53*, 3288–3291) precipitate the sodium as sodium zinc uranyl acetate at a temperature below 20° C. The uranium content of the precipitate is determined by titration with standard solution of sodium hydroxide, using phenolphthalein as the indicator. The sodium content of the precipitate is then calculated.

J. S. H.

Molecular Statistics of Enzyme Action. J. B. S. HALDANE (*Proc. Royal Soc.*, 1931, *B 108*, 559–567) states that one molecule of the enzyme catalase, acting at a temperature of 0° C., catalyzes the decomposition of 200,000 molecules of hydrogen peroxide per second. The active intermediate molecule of catalase-hydrogen-peroxide has a mean life of 0.0000001 second.

J. S. H.

THE FRANKLIN INSTITUTE.

STATED MONTHLY MEETING, OCTOBER 21, 1931.

The regular monthly meeting of The Franklin Institute was called to order at eight-fifteen P.M. by the Chairman, W. Chattin Wetherill, Vice-President.

He immediately called upon the Secretary for a statement concerning the business of the evening. The Secretary reported that the minutes of the last meeting (the Medal Day Meeting) had already been published in full in the JOURNAL of the Institute and moved that they be approved as printed. There being no objection, the Chairman announced that this motion was adopted.

The Secretary announced that since the last meeting of the Institute in May, the following changes had taken place in the list of members: New members: two Resident Life, six Resident, four Non-Resident, one Student. He announced with extreme regret the deaths of two members of the Board of Managers—Mr. Edward H. Sanborn and Mr. Samuel T. Wagner; and of two Honorary Members of the Institute, Rear Admiral J. B. Murdock, U. S. N., who died last spring, and Mr. Thomas A. Edison, the great inventor, the first recipient of the Franklin Medal. In addition to these gentlemen, the Secretary announced, with deep regret, the deaths of fourteen other members.

The Secretary then reported upon the progress of the construction of the Benjamin Franklin Memorial and The Franklin Institute building. He stated that many contracts had already been executed, that the work of demolition now to be done had been completed, and that the excavations were practically sixty per cent finished. He remarked upon the favorable financial condition and expressed the belief that there was no reason that the portion of the building now being erected should not be ready for occupancy by January 1, 1933.

Announcement was also made by the Secretary of the election to the Board of Managers of The Franklin Institute of the Honorable George W. Pepper and Mr. Charles H. Ewing, to fill vacancies caused by death.

There being no further business the Chairman presented as the speaker of the evening Captain A. W. Stevens, Air Corps, United States Army. Captain Stevens outlined the photographic methods and materials used by him and his fellow workers in the photography of the army and then showed a superb collection of photographs taken by him from elevations ranging from five thousand to twenty-five thousand feet in height. The audience filled the hall to its capacity and was apparently completely absorbed in the quality of Captain Stevens' talk and the photographs.

At ten o'clock, in accordance with the request of the President of the United States, the lights of the building were extinguished for one minute, as a tribute to Thomas A. Edison. The meeting was then adjourned, with a rising vote of hearty thanks to Captain Stevens for his delightful talk.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 14, 1931.)

HALL OF THE COMMITTEE,
PHILADELPHIA, OCTOBER 14, 1931.

MR. HENRY B. ALLEN *in the Chair.*

The following report was presented for final action:

No. 2919: Work of Dr. J. B. Whitehead in Dielectrics.

This report, recommending the award of the Elliott Cresson Medal to Doctor J. B. Whitehead, of Baltimore, Maryland, "In consideration of his many original investigations of dielectric behavior and allied subjects," was adopted.

The following report was presented for first reading:

No. 2941: Improvements in the Field of Absorption Refrigeration.

GEO. A. HOADLEY,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, October 21, 1931.)

RESIDENT MEMBERSHIP.

MR. CHARLES H. EWING, Vice-President, The Reading Company, Philadelphia, Pa.

NON-RESIDENT MEMBERSHIP.

DR. GILBERT E. DOAN, Associate Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

TRANSFER RESIDENT TO RESIDENT LIFE

JOHN J. L. HOUSTON, Philadelphia, Pa.

CHANGES OF ADDRESS.

DR. LESLIE R. BACON, 314 Clearbrook Avenue, Lansdowne, Pa.
MR. HUGO BILGRAM, Moylan, Delaware County, Pa.
MR. C. O. BILLOW, 1212 Ashland Avenue, Wilmette, Illinois.
MR. GEORGE W. BIRCH, JR., 7427 Rogers Avenue, Upper Darby, Pa.
MR. FREDERICK M. BRIGHAM, Aldwyn Lane, Villa Nova, Pa.
MR. W. D. BRUCE, 55 Hanson Place, Brooklyn, N. Y.
MR. E. H. BURK, 531 Pelham Road, Germantown, Philadelphia, Pa.
MR. MILTON W. DEISLEY, 428 East King Street, Lancaster, Pa.
MAJOR THOMAS H. GRIEST, 1835 Arch Street, Philadelphia, Pa.
MR. G. R. HALL, 100 William Street, New York City.
MR. LINN HELANDER, 3100 Brownsville Road, Mount Oliver Branch, Pittsburgh, Pa.
MR. MAYO D. HERSEY, Vacuum Oil Company, Inc., Paulsboro, N. J.
DR. G. A. HOADLEY, Committee on Science and Arts, 37–39 North Seventh Street, Philadelphia, Pa.

DR. FRED W. KRANZ, 2527 West Drive, Fort Wayne, Indiana.
MR. A. S. KREBS, 2506 Willard Street, Wilmington, Delaware.
DR. G. C. KUESEL, Suite 2103, Aldine Trust Building, Philadelphia, Pa.
MR. J. MCGOWAN, JR., s. w. Corner Market and Second Streets, Camden, N. J.
MR. F. MACMURPHY, 513 Fair Oaks Avenue, Los Flores Apartments, South Pasadena, California.
MR. MATTHEW F. MAURY, 2215 Locust Street, Philadelphia, Pa.
MR. W. C. MELCHER, JR., Cramp Brass and Iron Foundries, Paschall Station P. O., Philadelphia, Pa.
MR. OTHMAR KARL MARTI, Allis Chalmers Manufacturing Company, Milwaukee, Wis.
MR. HERMAN A. METZ, 230 Fifth Avenue, New York City.
MR. DAVID P. MOORE, Optical and Acoustical Engineer and Patent Attorney, 320 East Forty-second Street, New York City.
MR. C. B. NEBLETTE, 73 Seneca Parkway, Rochester, New York.
DR. WAYNE B. NOTTINGHAM, 1 Hillside Place, Cambridge, Mass.
MR. HAVILAND H. PLATT, 1095 Park Avenue, New York City.
MR. SAMUEL E. POND, 3433 Plumstead Avenue, Drexel Hill, Pa.
MR. BERNARD RHODES, Stud Holme, 34 Trafalgar Street, Healey, Batley, Yorkshire, England.
MR. PHILIP X. RICE, 720 North Atherton Street, State College, Pa.
MR. FRANK H. ROGERS, I. P. Morris Corporation, Paschall Station P. O., Philadelphia, Pa.
MR. T. EDWARD ROSS, 2101 Packard Building, Philadelphia, Pa.
MR. A. F. SHATTUCK, 614 North Cannon Drive, Beverly Hills, California.
REAR ADMIRAL ELLIOTT SNOW, Apartment 652, The Westmoreland, 2100 California Street, N. W., Washington, D. C.
DR. JOHN F. STEVENS, Latrobe Apartments, Baltimore, Maryland.
MR. H. BIRCHARD TAYLOR, Paschall Station P. O., Philadelphia, Pa.
MR. PAUL E. TODD, 103 Broad Street, Warrensburg, Mo.
MR. HARRY R. VAN DEVENTER, 3 West 50th Street, New York City.
MR. R. J. WENSLEY, Westinghouse Electric and Manufacturing Company, Plane and Orange Streets, Newark, New Jersey.
MR. DAVID P. WHEATLAND, 133 Front Street, Marblehead, Mass.
MR. W. CHATTIN WETHERILL, Room 111 College Hall, University of Pennsylvania, Philadelphia, Pa.
MR. G. H. WOODROFFE, Reading Iron Company, 401 North Broad Street, Philadelphia, Pa.

NECROLOGY.

Mr. John Brock, Philadelphia, Pa.
Mr. M. J. Caples, Norfolk, Va.
Mr. B. Denver Coppage, Wilmington, Del.
Mr. Thomas A. Edison, Orange, N. J.
Rear Admiral J. B. Murdock, U. S. N., Danbury, N. H.
Professor S. W. Parr, Urbana, Ill.
Mr. Fred A. Riehle, Philadelphia, Pa.
Mr. Morris Rosenbaum, Philadelphia, Pa.

LIBRARY NOTES.

RECENT ADDITIONS.

ALBERT, ARTHUR LEMUEL. The Fundamental Theory of Electrical Engineering. 1930.

American Concrete Institute. Proceedings. Volume 27, 1931.

American Gas Association. Proceedings. Twelfth Annual Convention. 1930.

DÉJARDIN, GEORGES. Les Quanta. 1930

DREYFUS, ROBERT. La Téléphonie. 1931.

LUCKIESH, M., AND FRANK K. MOSS. Seeing. A Partnership of Lighting and Vision. 1931.

MACDOUGAL, D. T. The Green Leaf. The Major Activities of Plants in Sunlight. 1930.

MOULTON, FOREST RAY. Astronomy. 1931.

National Research Council. Physics of the Earth. Volume 2, The Figure of the Earth. 1931.

RIBAUD, GUSTAVE. Traité de Pyrométrie Optique. 1931.

SCOTT, WILFRED W. Essentials of Quantitative Chemical Analysis. 1931.

STEWART, ALFRED W. Recent Advances in Organic Chemistry. Sixth edition. Two volumes. 1931.

TWYMAN, F., AND D. M. SMITH. Wave-length Tables for Spectrum Analysis. Second edition. 1931.

Who's Who in Engineering: a Biographical Dictionary of the Engineering Profession. Third edition. 1931.

BOOK REVIEWS.

TRAITE DE PYROMÉTRIE OPTIQUE, par Gustave Ribaud, Professeur à la Faculté des Sciences de Strasbourg, Directeur du Laboratoire de Pyotométrie de la Fondation Edmond de Rothschild. Préface de M. Charles Fabry, Membre de l'Institut. xvi–452 pages, 8vo, cloth. Paris, Editions de la Revue d'Optique Théorique et Instrumentale, 1931. Price 95 francs.

Over a long term of years engineers and physicists have steadily advanced the state of the art of high and low temperature measurements both in its practical aspects and from thermodynamic considerations. As a means of extrapolating the thermometric scale, the gas thermometer first, the electric resistance element and thermocouple thermometers, and finally visible and total radiation pyrometers have come into use. Unfortunately, the elements of resistance and thermocouple pyrometers have proved subject to many irregularities at high temperatures, and investigations in recent years have been directed to the more promising method of the properties of optical radiation which are governed by the famous Wien-Planck law of black body radiation which places the estimation of temperature upon a rationally deductive basis.

Professor Ribaud covers the development and analysis of the theoretical and practical aspects of radiation pyrometry with unusual thoroughness and copious documentation. About one half of the work relates to analytical and experimental investigation of principles, much of it from the records of the Bureau of Standards.

The remainder applies more specifically to the application of these principles to the different forms of optical pyrometers which have come into use with a searching examination of their advantages and limitations.

The treatise is one of rare value both as an exhaustive presentation of temperature measurement by radiation and as a copious source of systematic documentation.

LUCIEN E. PICOLET.

DIELECTRIC CONSTANT AND MOLECULAR STRUCTURE. By Charles Phelps Smyth, Associate Professor of Chemistry in Princeton University. American Chemical Society Monograph Series. 214 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1931. Price $4.00.

This book should hold more than ordinary interest for the organic chemist. The rapid development of physical chemistry in the last two decades has evolved many theories and methods for studying the physical properties of chemical substances. These methods have proved to be of immense aid to the worker in organic chemistry, in his task of identification as well as the determination of constitution and structure.

In "Dielectric Constant and Molecular Structure" the author, Charles P. Smyth, has succeeded in making a very thorough survey of this field which holds for him such keen interest. He has carefully weighed the relative importance of the mathematical experimental, theoretical and data interpretational phases of his subject. As a result, we have a book which quite candidly points out that, even if "dielectric constant" data have not succeeded in clearing up many important questions of chemical compound structure, the results at least have helped to make it more complicated.

The book logically starts out with a chapter on the "Mathematical Theory of the Dielectric Constant" in which the relation between dielectric constant, refractive index, electric moment and polarization is pointed out. Related to these Dielectric Constant and Electric Moment manifestations are such phenomena as the anomalous dispersion of radio frequencies by liquids and solids, electric double refraction in gases and liquids; electrostriction, a remarkable phenomenon shown by gases under the influence of an electric field, consisting of a contraction in volume or decrease in pressure. Polar compounds show other interesting evidences of their constitution through dipole rotation effects (rotation of a liquid by a rotating electric field) and molecular beams deflected by similar, stationary fields. Three principal methods of measuring dielectric constants are described, the more important ones being treated in considerable detail.

The chapter on "The Relation of Electric Moment to Molecular Structure" indicates the dependence of electric moment upon the structure of the molecule and points the way for the utilization of such data in the determination of this structure. In conclusion to the chapter on "The Electric Moments of Molecules and Radicols" the author points out that the introduction of an atom or group of atoms into a molecule may produce an electric moment which will be influenced by the nature of the rest of the molecule. Investigations of the organic cyclic compounds indicate the apparent absence of electric moment in benzene, diphenyl and naphthalene. Hence, it is to be concluded these substances are symmetrical in structure while the moments of the derivatives of benzene indicate this molecule

to have a plane hexagonal structure. Apparently there is very little connection between the electric moment of a molecule and its chemical activity. The chapter on "Electronic and Atomic Polarization" deals for the most part with the molecular, atomic and ionic refractions for vibrations in the range of visible light, the relation between these polarizations and the molecular refraction being very definitely defined. In the study of molecular association, polarization measurements have disclosed many anomalies in the behavior of certain alcohols. At the moment such results have rather complicated the theories on the phenomena of association but they no doubt will be of immense value in the search for the true explanation. The book is provided with an appendix containing a list of chemical compounds and their electric moments.

T. K. CLEVELAND.

THE FUNDAMENTAL THEORY OF ELECTRICAL ENGINEERING. By Arthur Lemuel Albert, M.S., Assistant Professor of Electrical Engineering, Oregon State College, ix–323 pages, illustrations, tables, diagrams, 8vo. Boston, Ginn & Company. Price $3.20.

The great strides in the technique of telegraphy, and telephony, the multiplicity of devices for railway train control, radio and other newcomers in the electrical industry have brought new interests into the field of technical education. Some of these advances have come about from new developments of fundamental electrical theory, but they cannot all be included as major topics in a four-year course in electrical engineering which is already very much occupied with the consideration of motors, generators and equipment for the control and transmission of current. Power is fundamental in all applications of electricity so that the principles which apply to electric power serve the student well also in the special industries which have only latterly achieved commercial importance. These specialties, the author says, can best be pursued by service in these industries. Accordingly, he has dealt fully only with fundamental electrical phenomena without overemphasizing their application to particular branches of electrical engineering. Besides the conventional topics of the principles of direct and alternating current theory, thermionic devices have been briefly treated in the chapter on the conduction of electricity through gases. The chapters on the theories of electricity, and on the dielectric circuit are also in harmony with modern views of the subject. The large number of well-chosen examples and the numerous references for collateral reading add materially to the value of this lucid and well arranged text.

LUCIEN E. PICOLET.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 394, Airship Model Tests in the Variable Density Wind Tunnel, by Ira H. Abbott, 24 pages, illustrations, quarto, Washington, Government Printing Office, 1931, price twenty cents.

An investigation of the aerodynamic characteristics of airship models was made in the variable density wind tunnel of the Committee. Eight Goodyear-Zeppelin airship models, supplied by the Bureau of Aeronautics of the Navy Department, were tested in the original closed-throat tunnel. After the tunnel was rebuilt with an open throat a new model was tested, and one of the Goodyear-

Zeppelin models was retested. These tests were made at tank pressures varying from 1 to 20 atmospheres, and the extreme range of Reynolds Number was about 1,000,000 to 40,000,000. The lift, drag, and moment coefficients of the models were determined, and the effects upon these coefficients of pitch, fineness ratio, scale, surface texture, initial degree of air-stream turbulence, and the effects of the addition of fins and cars were investigated. The resulting curves are included.

The results show that the addition of fins and car to the bare hull of a model causes an increase in lift at positive angles of pitch and causes an additional drag which increases with the pitch. Little change in drag coefficient was found between a fineness ratio of about five and seven. The effect of surface roughness on drag was found to be very large. The drag coefficient and the apparent effect of scale depend upon the initial degree of air-stream turbulence. The results indicate that much may be done to determine the drag of airships from evaluations of the pressure and skin-frictional drags on models tested at large Reynolds Numbers.

Report No. 395, A New Principle of Sound Frequency Analysis, by Theodore Theodorsen, 15 pages, illustrations, quarto, Washington, Government Printing Office, 1931, price fifteen cents.

In connection with a study of aircraft and propeller noises, the Committee has developed an instrument for sound-frequency analysis which differs fundamentally from previous types, and which owing to its simplicity of principle, construction, and operation, has proved to be of value in this investigation. The method is based on the well-known fact that the ohmic loss in an electrical resistance is equal to the sum of the losses of the harmonic components of a complex wave, except for the case in which any two components approach or attain vectorial identity, in which case the ohmic loss is increased by a definite amount. This fact has been utilized for the purpose of frequency analysis by applying the unknown complex voltage and a known voltage of pure sine form to a common resistance. By varying the frequency of the latter throughout the range in question, the individual components of the former will manifest themselves, both with respect to intensity as well as frequency, by changes in the temperature of the resistance. This principle of frequency analysis has been presented mathematically and a number of distinct advantages relative to previous methods have been pointed out. Among these is the fact that the frequency discrimination or resolving power is inherently large and remains constant for the entire working range. No difficulties exist as to distortions of any kind. The fidelity of operation depends solely on the quality of the associated vacuum-tube equipment

An automatic recording instrument embodying this principle is described in detail. It employs a beat-frequency oscillator as a source of variable frequency. A large number of experiments have verified the predicted superiority of the method. A number of representative records are presented.

BULLETIN OF THE NATIONAL RESEARCH COUNCIL, Number 78—Physics of the Earth II, The Figure of the Earth, a collection of short papers written by leading scientific men in several branches of geophysics, and treating of the size and shape of the earth, 286 pages, illustrations, 8vo. Washington, National Academy of Sciences, 1931. Price $3.50.

Students of geophysics will find this compendium particularly interesting. The several papers prepared by men, authorities in their several fields, give the

lay reader insight into the present problems of the earth's figure. This achievement should satisfy the fond wish of Dr. J. S. Ames who was so tireless in promoting the Physical Sciences as chairman of that division of the National Council.

Statisticians assure us that figures never lie. Geophysicists are not so reassuring about the figure of mother earth. One feels very unsteady after reading of the movements of isostasy while the surge of the tides not only on the sea but also the land leave one with a very present sense of nausea. One at least realizes the loose meaning of sea-level which should be reduced to a mean sea-level for purposes of careful measurement. No brief statement can do justice to the abundance of careful work behind these papers that not only tell of the gravity and tides of the earth but also of the forces of equilibria which urge and restrain a spinning mass of varied density and uneven surface—the earth on which we live, in a fancied security.

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PUBLICATIONS RECEIVED.

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CURRENT TOPICS.

Microscopic Organisms Aid in the Natural Purification of Streams—(*United States Public Health Service*). Where reedbirds and ducks are found in abundance in their natural feeding grounds, or where buzzards are seen circling low, it is known that they are attracted by the presence of food. In somewhat similar fashion certain microscopic animals are attracted by the presence of organic matter found in sewage, which serves as their food. Where these organisms are found, it is known that the water is polluted, for they will disappear, like buzzards, when their food supply is exhausted. These minute organisms, which together with certain other microscopic forms of life, both animal and plant, are collectively called plankton, and they play a very important role in the process of natural purification of streams, the minute animals feeding upon the polluting organic wastes, and the microscopic plants giving off oxygen.

The much-discussed Illinois River, heavily polluted by the sewage and stockyard waste from Chicago, was used by the Public Health Service for a study of the effect of these microscopic organisms on nature's methods of purification of streams and a report (Public Health Bulletin No. 198) dealing with this particular study has recently been published.

Approximately 1,000 weekly samples, collected at every season, and including all sections of the river (which is nearly 300 miles long), were analyzed and studied. Particular information was sought relative to the abundance of such organisms as thrive in sewage-polluted water, and their gradual replacement downstream by organisms known to require water of a better grade. The gradual purification of the stream was thus expressed in terms of the prevalent kinds of microscopic organisms, both plants and animals, and collectively known as Plankton. The relative abundance of microscopic green plants was a matter of interest, inasmuch as these plants help to purify the water by the oxygen they give off, similar to the action of the common " fish moss " in goldfish bowls.

Very briefly summarized, the results of this study indicate the following changes as the water progresses:

1. The swift upper portion of the river, heavily polluted but thoroughly mixed, is well seeded at the start with microscopic organisms from the tributary Des Plaines River and from Lake Michigan.

2. Gradually decreasing velocity distributes the suspended matter over a very large total area of bottom downstream, facilitating biological action.

3. The grayish water becomes clear, and loses its odor of sewage 70 or 80 miles downstream from the Chicago Drainage Canal outlet.

4. Correlated changes in the plankton content are: (*a*) Decrease of pollutional organisms formerly predominant, (*b*) increase of organisms of the cleaner-water kinds, these becoming predominant, and maintaining this status thereafter, and (*c*) increase in relative abundance of microscopic green plants.

5. In all sections of the river, and at all seasons, the microscopic green plants were decidedly more abundant, volume for volume, than were the microscopic animals.

6. Malodorous bottom sediments from the polluted upper Illinois contained very large numbers of "sludge worms," and no gill-bearing insect larvae, whereas sediments from the lower portions of this stream were free of odor, contained very few worms, and showed a variety of gill-breathing insect larvae.

A suitable background for the above study is furnished by eleven abstracts of similar studies made on other streams and on the Illinois River by various investigators. The large amount of data relative to the Illinois River is summarized in 54 tables and 18 graphs. There are also a number of photographs showing field conditions, and some photomicrographs of the more important plankton organisms. R.

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